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An Alternative Approach to Estimating Supply Response of a Perennial Crop

HABIBAH SULEIMAN

In previous studies on natural rubber supply, lags have often been incorporated in economic and econometric models designed to explain the dynamic supply response. These lags in input and output prices have not, however, reflected directly the restrictions involved in the growth process for rubber trees. Often these lag structures have been superimposed on models based on static economic theory rather than being based on dynamic economic theory. The phenology for tree crops plays a valuable role in the determination of output levels and supply response. In this paper, the foundation of the supply response specification for rubber is the theory of adjustment cost where the production function incorporates the investment rather than the price expectation model. This was reflected in the results obtained from the impact multiplier and sensitivity analysis. The incorporation of prior information or the phenological process together with economic structure improves the dynamic property of the model.

Several distinct stages of production are involved in the supply of perennial crops. As in the livestock industry, where the biological nature of the animals provides important *a priori* information, in the estimation of supply, the phenological structure of the tree crops plays a unique role in the determination of output supply. Previous studies on NR recognised the fact that the supply response involved a dynamic process. The theoretical inclination of these studies in describing the dynamic process was the backward looking expectation model with no reference to the underlying production function¹⁻⁴, often resulting in some form of distributed lag model. Later studies did use some form of dynamic optimisation theory⁵⁻⁸.

The objective of this paper is to illustrate that the incorporation of the phenological structure of a perennial crop provides useful information in the formulation of lags in the dynamic supply functions.

THEORETICAL JUSTIFICATION/CONSIDERATION

Static economic theory is rich and abundant. However, the same can not be said of the dynamic theory of economic behaviour.

Economic decisions and their implementation are not required to be instantaneous. In the dynamic models for example, the response of a physical investment is not assumed to be achieved instantaneously but rather distributed over a number of years. Thus, lags are often appropriate in economic and econometric models designed to explain the dynamic supply response. Often these lag structures are superimposed on models based on the static theory rather than on the dynamic theory⁹.

The dynamics of supply response have been treated in two ways. Firstly, it has been analysed using the expectation and partial adjustment models of Koyck and Nerlove. However, this approach is limited to explaining the dynamics, in that expectations are formulated not only on past but also on future events. Problems are associated with the implied dynamic behaviour¹⁰. Secondly, the dynamics of supply response has been approached by using the dynamic optimisation theory *via* the adjustment cost. In this study, the output supply and input demand functions are derived from the production function. Besides this, the investment flow concept is incorporated into the analysis to reflect the dynamics of the production process. In addition to the above two approaches, it is

*Malaysian Rubber Research and Development Board, P.O. Box 10508, 50716 Kuala Lumpur, Malaysia

forseeable that the dynamics of the production process can be recast by incorporating the adjustment cost and forward-looking expectation models. Thus, production function, investment and price expectations are important influencing elements in the formulation of dynamic supply response. What has usually been used in applied work is an unrestricted reduced form which attempts to capture all these effects. The theoretical bias of the dynamic supply function for rubber is the second approach.

Adjustment Cost Approach

Recent development of the dynamic theory has made *ad hoc* approaches to dynamic analysis of supply no longer necessary. The theory of adjustment cost has been used to provide a consistent framework for input demand and output supply¹¹⁻¹⁵. Implications for the demand and supply functions of a firm maximising discounted profits and facing changing adjustment costs can be viewed as the 'close loop' solution to an intertemporal profit maximisation problem. Although approaches to dynamic optimisation differ, the basic approach in the theory is the same. The production function incorporates adjustment costs and the firm is assumed to maximise the present value of the objective function over a finite or infinite horizon. In all but the most specialised circumstances, price expectations are taken as fixed or assumed to be static.

Firm level. Assume that a price taker firm has a production function

$$Q = F [X_1(t), X_2(t)] \quad \dots 1$$

where X_1 is labour (the variable factor) and X_2 is capital (the fixed factor or factor requiring adjustment cost). The capital stock, is determined by

$$\dot{X}_2 = \frac{dX_2}{dt} = I - \delta X_2(t) \quad \dots 2$$

where δ is the depreciation rate and I is gross investment. The initial capital stock is taken to be $X_2(0)$. If the user cost of capital or the rental price is $v(r + \delta)$, the present value is

maximised by a policy that maximises the expression

$$P.F[X_1(t), X_2(t) - WX_1(t) - v(r + \delta)X_2(t)0] \quad \dots 3$$

for each point of time in $t > 0$. The optimal capital stock, X_2 will then be held for all $t > 0$ if the *Function 3* is maximised. With the labour variable and capital quasi fixed and gross investment taking place, the cost per unit of gross investment assumed an increasing function of the rate of investment or internal cost in terms of output foregone must be introduced. Thus, the production *Function 1* is replaced by

$$Q(t) = F[X_1(t), X_2(t), I(t)] \quad \dots 4$$

The maximum problem of the firm is then recast as

$$V(0) = e^{-rt} \int_0^{\infty} [P.F[X_1(t), X_2(t), I(t)] - WX_1(t) - vI(t)] dt \quad \dots 5$$

where F is assumed homogeneous of degree one with continuous first and second derivatives having the necessary regularity conditions and qualitative restrictions. Then, the optimising problem of the firm can be written as

$$\text{Max } V = \int_0^{\infty} (PQ - WX_1 - vI)e^{-rt} dt \quad \dots 6$$

$$X_1(t), X_2(t) \geq 0$$

$$\text{subject to a) } \left. \begin{aligned} Q &= F(X_1, X_2) - C(X_2), \text{ where } C \text{ is} \\ &\text{the adjustment cost,} \\ &F(I, X_2) \end{aligned} \right\} \dots 7$$

$$\text{b) } \left. \begin{aligned} X_2 &= I - X_2, \\ X_2(0) &= X_2 \end{aligned} \right\}$$

$$\text{c) } X_1, X_2 > 0$$

The subscript t has been omitted for convenience. The problem on *Equations 6* and *7* is amiable to the solution by the calculus of variations. Specifically, the Hamiltonian for *Equations 6* and *7* is

$$H[I, X_1, X_2, \lambda] = e^{-rt} [PF(X_1, X_2, I) - PF(I, X_2) - WX_1 - vI - \lambda(I - X_2)] \quad \dots 8$$

The term $\lambda(I - X_2)$ adjusts for the fact that the present value of the activities taking place at time t , should reflect the value of later

product due to investment activities in period t . Necessary conditions¹² for maximising Equation 8 are

$$\left. \begin{aligned} \text{i) } \dot{X}_2 &= I - X_2, X_2(0) = X_2 \\ \text{ii) } \partial H / \partial X_2 &= -PF_2(X_1, X_2, I) \\ &\quad - PF_1(I, X_2) \\ &\quad - (r + \delta) \lambda \\ \text{iii) } \partial H / \partial X_1 &= 0 = PF_1(X_1, X_2) - W \dots 9 \\ \text{iv) } \lambda &= v + PF_1(I, X_2) \\ \text{v) } \lim_{t \rightarrow \infty} e^{-rt} &= 0 \\ \text{vi) } -PF_1(I, X_2) e^{-rt} &< 0 \end{aligned} \right\}$$

Condition (iii) has the familiar interpretation, a variable factor will be utilised until its value of marginal product is equal to its unit cost. This condition holds for every time period since all the variables are functions of time as opposed to static theory where the condition holds *rata* a single point of time. In Condition (ii), $\lambda(t)$ is the discounted value at t of the alter marginal product of capital and with Condition (iv), it requires that t be equated to its marginal cost which is determined by v , the cash outlay per unit of investment goods and PF which is the value of output foregone. Conditions (ii) and (iv) and the term $r + \delta$ convert a stock price to a flow price and thus introduce a flow or investment decision into the analysis. Conditions (ii), (iii) and (iv) can be written as;

$$\begin{aligned} PF_1(X_1, X_2) &= W \dots 10 \\ PF_2(X_1, X_2, I) &= -PF_1(I, X_2) \\ &\quad - (r + \delta)v + \\ &\quad (r + \delta) PF_1 \\ &\quad (I, X_2) \\ &= (r + \delta)v - \\ &\quad PF_1(X_1, X_2) \\ &\quad (r + \delta) \\ &= (v - PF_1) \\ &\quad r + \delta \dots 11 \end{aligned}$$

Equation 10 is the marginal productivity condition for labour (the variable input). Equation 11 is the optimal behaviour where the marginal value product of capital is equated to the marginal cost of accumulating capital ($v - PF_1$) but in the dynamic case it incorporates the flow of investment decision as represented by $(r + \delta)$.

Firm level input demand and output supply. The input demand for labour and output supply of the firm can be derived from Equations 2, 10 and 11. Since F is homogenous of degree one, its derivatives are homogenous of degree zero and thus can be written as functions of the ratios X_1/X_2 and I/X_2 . From Equation 10, the demand for labour is determined by

$$\begin{aligned} PF_1(X_1, X_2) &= W \\ \text{or} \\ X_1 &= X_2(t), D^*_1 W/P \dots 12 \end{aligned}$$

i.e., demand for labour is a function of capital, price of the output and its own price.

For the investment demand, Equation 11 can be rearranged as

$$\begin{aligned} PF_2(X_1, X_2, I) + PF_1(I, X_2) \\ (r + \delta) &= v(r + \delta) \dots 13 \end{aligned}$$

Applying Euler's Theorem to F and using Equation 12 to eliminate X_1/X_2 ,

$$\begin{aligned} PF_1[I, D_1 W/P, I/X_2] - \\ D_1(W/P) W/P + (r + \delta - I/X_2) \\ F_1(I/X_2) &= v(r + \delta) \dots 14 \end{aligned}$$

Let the left hand side of the equation be represented by $G(I/X_2, W, P)$, then

$$PG(I/X_2, W, P) = v(r + \delta) \dots 14$$

If P is greater than a critical value P_c , investment demand can be solved from Equation 14;

$$I(t) = X_2(t), D_2(W/P, v/P, r, \delta) \dots 15$$

Investment demand is a function of capital stock, price of the variable input, price of the output, rate of discount, depreciation rate and cash outlay per unit of investment.

Substituting $X_1(t)$ and $I(t)$ into the production function, the output supply for the firm is

$$\begin{aligned} Q(t) &= X_2(t), F(1, D_1 W/P, \\ &\quad D_2 W/P, v/P, r, \delta) \dots 16 \end{aligned}$$

The firm's supply in relation to output and input demand depends on prices in ratio forms only and on present stock of capital (also on earlier investments). For example, optimising perennial crop output depends not only on the

existing stock of capital (the stock of trees) but also on the investment in new trees. For long-run supply response, assuming that the price is maintained over the relevant time period, the supply output is given by the time path of $X(t)$

$$\begin{aligned} \dot{X}_2(t) &= I(t) - X_2(t) \\ &= \delta X_2(t) D_2(W/P, v/P, \delta, r) \\ &\quad - \delta X_2(t) \end{aligned} \quad \dots 17$$

$$X_2(t)/\dot{X}_2(t) = D_2(W/P, q/P, \delta, r) - \delta$$

From *Equation 17* under this constant price scenario, gross investment, labour force utilisation and output¹¹ will grow at a rate $D - \delta$.

Industry level. In dynamic theory, the supply of output and input demand of an industry takes into consideration whether there will be entry into the industry. Assuming there is no entry, the firms face an identical set of production functions and prices. The industry demand function is

$$D(t) e^{-rt} = Q(t) - h[P(t)] \quad \dots 18$$

where $h'(P) < 0$, $h(0) = \infty$, $h(\infty) = 0$. The shift in demand, for example, is due to growth in income (θ), and the growth rate in output is given by the right hand side of *Equation 18* and further assuming that market clearance occurs at each point in time, the industry supply function is

$$Q(t)/\dot{Q}(t) = g[P(t) - \theta] \quad \dots 19$$

With entry of firms, the present value of capital under optimal policy, $V^*[X_2(0)/X_2(0)]$, is not equal across the industry but should be a rising function of this ratio. For fixed factor prices, $V^*[X_2(0)/X_2(0)]$ will be an increasing function of the output price P . If $g(P)$ and $g'(P) > 0$, the increase in output from new firms will alter *Equation 18* to

$$Q(t)/\dot{Q}(t) = g[P(t) + g'[P(t)] - \theta] \quad \dots 20$$

The industry's gross investment demand can be obtained by aggregating *Equation 15*, a function of output price and other variables, *i.e.*

$$I(t)/X_2(t) = D_2(r, W/P, q/P) \quad \dots 21$$

As mentioned earlier, an assumption made in the adjustment model is static expectation. This results in the investment demand of *Equation 15*. The process by which price expectations are formed and how the process is related to other decisions of the firm are important in understanding the investment demand. If the weighted average of current prices and prices previously are expected to prevail (similar to that of Koyck and Nerlove), then price expectation behaviour introduces lagged input prices into the investment model. Of course, the inputs in production function determine the prices entering the investment relationship. The reliance of price expectation behaviour on current *versus* past prices determines whether these input price variables enter as lagged or in current values. Thus, the formation of price expectations can be important in developing dynamic models of the firm.

EMPIRICAL ANALYSIS

The foundation of the supply response for rubber is based on the theory of adjustment cost where the production function incorporates the investment flow concept rather than the price expectation model. Additionally, the theory suggests the incorporation of the phenological structure of the production process.

Production occurs over a number of years involving important lags in the process. The phenological relationships between planting, maturity and removal provide important *a priori* information for the study of supply responses. According to the dynamic theory, this information enters in the form of physical accounting relationships and is critical in the determination of the supply of rubber. The phenological relationships provide valuable constraints for the economic stimuli that are presumed to influence supply responses.

PHYSICAL OR PHENOLOGICAL RELATIONSHIP

Stocks and Flow Relationship

The inter-relationship between the various stages of production can be found from the

acreage data for rubber in Peninsular Malaysia. These data are divided into planted, mature and immature, new plantings and replantings, and tapped area. No information is available on removals.

Mature area can be interpreted as the productive capacity or the stock of rubber trees and new plantings as the flow or investment that determines the stock. The relationships between these stocks and flows can be written as

$$MA_t = MA_{t-1} + NP_{t-6} - REM_t \quad \dots 22$$

and

$$REM_t = NP_{t-30} \quad \dots 23$$

where MA_t is mature area in the current period

MA_{t-1} is mature area in the previous year

NP_{t-6} are new plantings lagged six years

REM_t is the current removal.

Thus, mature area in the current year is equal to mature area last year plus the net addition, that is the difference between the new mature area and the area that is removed. It is assumed in *Equation 23* that trees reach maturity on the seventh year and are removed after thirty years¹⁶. Thus, *Equation 23* unlike *Equation 22* is an assumption not an identity.

Recall that no data are available on removal. However, from the assumption in *Equation 23*, REM^*_t can be calculated as

$$REM^*_t = MA_{t-1} - MA_t + NP_{t-6} \quad \dots 24$$

that is REM^*_t is the residual. Of course, *Equation 22* can be re-written as

$$MA_t = MA_{t-1} + NP_{t-6} - REM^*_t \quad \dots 25$$

and hold exactly, given that removal in period t is residually determined as assumed.

In *Equation 25*, the important variable is NP_{t-6} as it determines the amount of land available for replanting thirty years hence. It is a constraint faced by the estate sector, in particular. The amount of land available for

replanting is a function of removals. Land is controlled by the various state governments and several restrictions are imposed on the acquisition of new land by the estates. The effect is to hold the land base of the estates relatively constant, at least in the short run.

The ratio NP_{t-6}/REM^*_t indicates the land for replanting or new planting. For the estate sector, the average value of the ratio was 0.7213 although over the sample period the value declined from 1.0 in 1952 to 0.53 in 1980. For the smallholders, the average value of NP_{t-6}/REM^*_t was 13.763. This large value is not surprising. Government agencies were actively involved in encouraging new plantings and replantings and, more generally, the growth in natural rubber production in this sector¹⁶.

Several other useful relationships can be derived from *Equation 25*

$$MA_t - MA_{t-1} = NP_{t-6} - REM^*_t \quad \dots 26$$

or

$$MA_t - MA_{t-1} = (NP_{t-6} - REM_t) + (REM_t - REM^*_t) \quad \dots 27$$

From *Equations 26* and *23*, the difference in mature area is equal to the net addition plus the difference between removal from 'long term' trend as defined in *Equation 23*. If $REM_t = REM^*_t$, the area removed is equal to area planted thirty years earlier. If the difference is positive then less area is being removed or there is a slow down in the removal process. Thus, $REM_t - REM^*_t$ can be interpreted as the 'discretionary removal' — the variable that reflects the absence or presence of new investment when attractive or unattractive incentives are provided.

Ratios of stocks to flows. Before further developing the analysis of supply based on the ratios, it will be useful to examine more completely the physical lags and relationships in rubber production. It takes on the average six to seven years for an area planted with rubber to mature. Trees are kept until they are about thirty years old after which they are removed and the area replanted with rubber or other competing crops.

Using Equation 25, several ratios of stocks to flows can be calculated. It is not true to assume that the addition to the mature area will be the area planted six years ago. Losses due to death and other economic factors have to be considered. Only a proportion (δ) of the area planted six years ago will be added on to the existing mature area. Thus,

$$MA_t = MA_{t-1} + NP_{t-6} - REM^*_t \quad \dots 28$$

and

$$\frac{MA_t - MA_{t-1} - REM^*_t}{NP_{t-6}} \quad \dots 29$$

Yearly values of δ along with the standard deviations are summarised in Table 1. The value of this ratio together with the identity form the physiological basis for the supply response model. One would not expect this ratio to be constant over time. For example, the period of immaturity is likely to be shortened (lengthened) when prices are high (low) due to the opportunity cost involved.

PHENOLOGICAL MODEL

Using the average values of $\hat{\delta}$ derived from above, a simple or naive model for mature area is specified. This model does not include the economic variable *i.e.* the price. The model and the derived values are used primarily to indicate the importance of the successive stages in the production process for supply. Knowledge of this information is useful in the supply response analysis.

Based on the premise that only a proportion of new planting will mature, the mature areas for both sectors can be derived by substituting the average values of δt , $\hat{\delta}$, into Equation 28 *i.e.*

$$MA_t = MA_{t-1} + NP_{t-6} - REM^*_t \quad \dots 30$$

Using Equation 30, the mature area data series were generated.

Specifically, Figures 1 and 2, show the historical and data series as generated. The results obtained are surprisingly good. For both sectors the naive model tracks the historical series well. Deviations are expected as the influence of economic variables has not been taken into consideration. The incorporation of price and other economic effects into the supply response model will improve the tracking performance.

ECONOMIC ASPECTS OF SUPPLY RESPONSE

The phenological structure of this perennial crop is, clearly from the above, a major determinant in the production dynamics. No fully dynamic theory can determine the supply response without utilising these inherent characteristics. The economic variables are included to explain the variations from the long-term stock flow averages. Thus, economic variables are included to explain the variations other than long-term averages. Economically motivated behavioural equations are formulated for explaining these deviations from the ratios based on the theoretical results above.

Behavioural Equation

Based on the dynamic theory, supply responses depend not only on present stock of capital but also on earlier investments. Investment in this instance is new planting (*NP*) and the stock of capital is mature area (*MA*). Investment demand, in turn, is postulated to be the function of existing capital stock, the price of input, the price of output, the rate of discount, the cost of investment and relevant variables. Prices are introduced in ratio form only. Thus, *NP*, in the present analysis is

TABLE 1. YEARLY RATIOS OF STOCK TO FLOW

Sector	Mean	Standard deviation	Minimum value	Maximum value
Estate	0.696	0.439	-0.354	1.573
Smallholder	0.836	0.527	-0.140	2.439

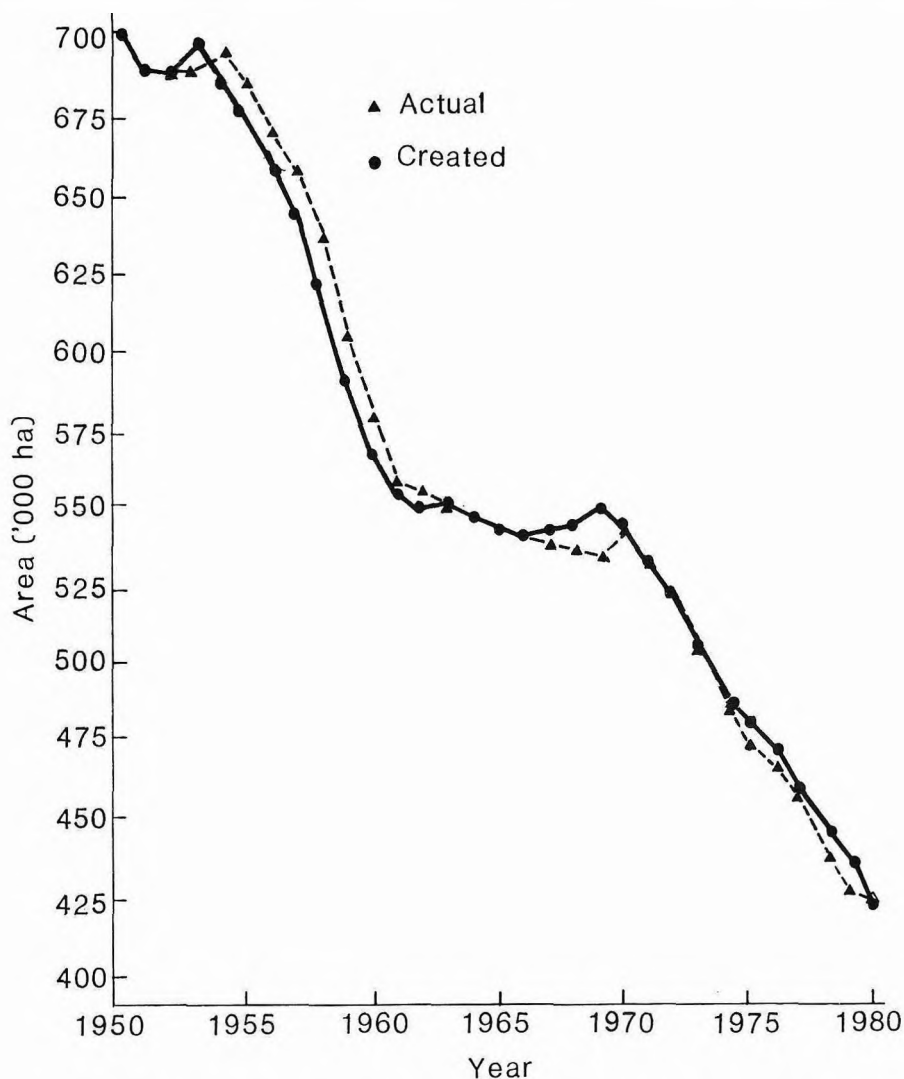


Figure 1. Plot of historical mature area and mature area created for estate sector.

hypothesised as a function of the price ratio of rubber to palm oil, the ratio of input price (namely wages), the cost of investment proxied by the discount rate, the lagged removals and new plantings. More specifically, the equations are;

$$NP_t^E = f_1(PR_t, PR_{t-1}, NP_{t-1}, REM_{t-1}, WP_t, IP_t) \dots 31$$

and

$$NP_t^S = f_2(PR_t, PR_{t-1}, NP_{t-1}, RP_t) \dots 32$$

NP_t^E , and NP_t^S , are differences from long-term averages of new plantings for estates and smallholdings, respectively. In Equations 31 and 32, PR_t and PR_{t-1} are the price ratios of RSS 1 (the noon rubber price in Kuala Lumpur) to palm oil current and lagged, WP_t is the ratio of wages to palm oil, IP_t is the ratio of discount rate to palm oil, NP_{t-1} and REM_{t-1} are new planting and removal, lagged one period. For the smallholder sector replanting grants, RP_t , is used as an explanatory variable. Past removal is not a determining

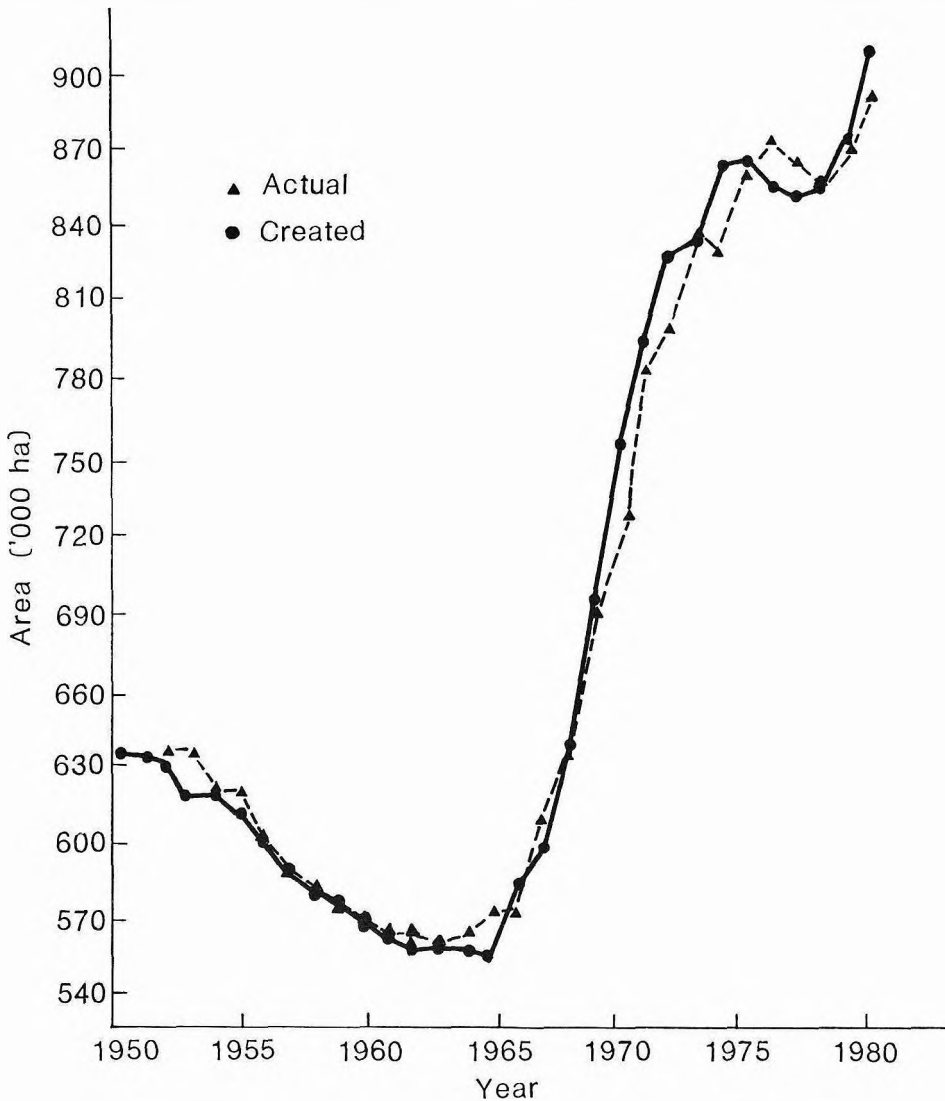


Figure 2. Plot of historical mature area and mature area created for smallholder sector.

factor in new planting for the smallholdings as compared with the estates since land is not constrained.

The flow of investment to existing stock of capital is determined by the phenological structure, namely δ . It can be observed that the ratio fluctuates from year to year. Fluctuations arise for several reasons; prices, land availability and its lagged value, thus, the variations in δ

is hypothesised to be the function of such variables, or more specifically,

$$\delta_t^E = f_1(\text{RSS } 1_t, \delta_{t-1}) \quad \dots 33$$

and

$$\delta_t^S = f_2(\text{RSS } 1_t, \text{REM}_{t-1}). \quad \dots 34$$

where E_t and S_t are differences from long-term averages of investment flow for the estates

and smallholdings respectively, while REM_{t-1} is removal for the last period.

Removals (REM) are hypothesised as a function of current and lagged prices, lagged mature area and its lagged value. The specifications are:

$$REM_t^E = f_1(RI_t, RI_{t-1}, REM_{t-1}, MA_{t-1}) \quad \dots 35$$

and

$$REM_t^S = f_2(RI_{t-1}, REM_{t-1}) \quad \dots 36$$

REM_t^E and REM_t^S are differences from long-term averages of removals for the estates and smallholdings respectively. For the smallholdings, it is hypothesised that removal is determined by persistence or past habits rather than economic variables as shown by Equation 36.

Empirical Estimates

The above specified behavioural equations were estimated using ordinary least squares for the period 1950 – 80. The use of OLS estimation was justified on the basis of its computational simplicity as well as the robustness of the parameter estimates. Table 2 contains the estimated parameters for Equations 31 – 36. The reported statistics include t values, R^2 and Durbin Watson h statistics. The ordinary Durbin Watson statistics is not applicable since these equations have lagged dependent variables as regressors.

Generally, the results are consistent with *a priori* expectation for the signs of the estimated coefficients. The coefficients of lagged values are positive and less than one indicating that adjustments to changes do not occur fully in the time frame of the model specification.

FULL SUPPLY RESPONSE MODEL

The supply response model for each of the sector consists of three structural equations and three identities. Specifically, for the estate sector the specification is:

$$MA_t^E = MA_{t-1} + SNP_t - REM_t \quad \dots 37$$

and

$$SNP_t = \delta \cdot NP_{t-6}$$

$$\delta_t^E = f(RSS\ I, \delta_{t-1}) \quad \dots 38$$

$$NP_t^E = g(PR_t, PR_{t-1}, NP_{t-1}, REM_{t-1}, IP_t, WP_t) \quad \dots 39$$

$$REM_t^E = h(RI_t, RI_{t-1}, REM_{t-1}, MA_{t-1}) \quad \dots 40$$

$$YIELD_t^E = \text{Average yield} \quad \dots 41$$

$$PRODUCTION_t^E = \text{Yield} \times MA_t \quad \dots 42$$

For the smallholder sector, the specification is:

$$MA_t^S = MA_{t-1} + SNP_t - REM_t \quad \dots 43$$

with $SNP_t = \delta \cdot NP_{t-6}$

$$\delta_t^S = f(RSS\ I, REM_{t-1}) \quad \dots 44$$

$$NP_t^S = g(PR_t, PR_{t-1}, NP_{t-1}, RP_t) \quad \dots 45$$

$$REM_t^S = h(RI_{t-1}, REM_{t-1}) \quad \dots 46$$

$$YIELD_t^S = \text{Average yield} \quad \dots 47$$

$$PRODUCTION_t^S = \text{Yield} \times MA_t \quad \dots 48$$

where all variables are as previously specified.

EMPIRICAL RESULTS

Using the regression results (Table 2), the full model was simulated. In the *ex-post* or historical simulation, the simulated model performed well. The simulation results showed a remarkable ability of the supply response model to reproduce the endogenous variables. This inaccuracy is likely to be due to the habit or persistent behaviour of the smallholdings making them less responsive to economic factors.

To calculate the price elasticity of the supply response, a restricted reduced form for the estimated structural equations was derived. The derived reduced form offers a means of more efficiently estimating these estimators¹⁷. The derived short-run and long-run price elasticities from the full model are shown in Table 3. The results obtained from these restricted reduced form specifications are comparable to those from past studies (Table 4). The estimated supply response is inelastic, as expected of a perennial crop, more so in the short run than in the long run.

TABLE 2. REGRESSION RESULTS FOR THE ESTATE AND SMALLHOLDER SECTOR

Dependent variable	Price and economic variables													Statistics		Equation No.
	Constant	RSS 1	REM _{t-1}	PR	PR _{t-1}	RP	IP	WP	MA _{t-1}	NP _{t-1}	δ_{t-1}	IR	IR _{t-1}	R ²	D.W.h	
δ^E	0.289314 (1.2433)	-0.000052 (0.4626)	—	—	—	—	—	—	—	—	0.71396 (5.0670)	—	—	0.507	0.5998	4.9
δ^S	0.917248 (2.3205)	-0.000066 (0.3491)	0.00236 (0.2678)	—	—	—	—	—	—	—	—	—	—	0.007	0.0808	4.10
NP ^E	1.178775 (0.1861)	—	0.04332 (0.2526)	1.33565 (1.8910)	0.77292 (0.9745)	—	-142.27422 (0.6871)	-16.43272 (1.0956)	—	0.60469 (3.6658)	—	—	—	0.879	0.7692	4.11
NP ^S	-9.95429 (0.1170)	—	—	0.675018 (0.4605)	0.36961 (0.3136)	0.32152 (0.2312)	—	—	—	0.78862 (6.3381)	—	—	—	0.7063	0.9705	4.12
REM ^E	12.4807 (0.8800)	—	0.5116 (3.4182)	—	—	—	—	—	0.01777 (1.0283)	—	—	-5.8047 (0.2369)	-29.9257 (1.1544)	0.6617	-1.1422	4.13
REM ^S	25.95214 (2.9024)	—	0.03589 (0.1654)	—	—	—	—	—	—	—	—	—	-31.1121 (0.7894)	0.0145	-0.0874	4.14

Figures within brackets indicate the *t*-statistics

TABLE 3. SHORT- AND LONG-RUN PRICE ELASTICITIES OF SUPPLY^a

Sector	Price elasticities of supply ^b	
	Short run	Long run
Estate	0.0153359	0.400607
Smallholder	0.0036091	0.013805

^a Calculated at the mean value

^b Inclusive of lagged price

Naive Model for the Smallholding

The economic variables used to explain the variations in *Equations 43* and *48*, of the smallholder sector did not contribute importantly to the explanatory power of the model. Thus, it was hypothesised that the production dynamics of the smallholding is best described as determined by purely phenological phenomenon. Using the long-term averages for δ and REM^S , the supply response model for the smallholder sector was re-specified as .

$$MA_t = MA_{t-1} + SNP_t - REM_t \quad \dots 49$$

$$\text{where } SNP_t = \delta NP_{t-6} \quad \dots 50$$

$$NP_t = f(PR_t, PR_{t-1}, NP_{t-1}, RP_t) \quad \dots 51$$

$$REM_t = 16.1956749 \quad \dots 52$$

$$YIELD_t = \text{Average yield} \quad \dots 53$$

$$PRODUCTION_t = \text{Yield} \times MA_t \quad \dots 54$$

This simplified model was then simulated. Interestingly, the *ex-post* or historical simulations for NP_t , MA_t , and $PRODUCTION_t$ performed just as well with the simplified model as with previous models that included economic conditioning variables.

MODEL EVALUATION AND POLICY SIMULATION

Ex-post simulations are useful in policy analysis. By changing values of selected exogenous variables or letting the exogenous variables follow a different time path, an examination and comparison of what might occur as a result of alternative policies can be undertaken. Impact multipliers are calculated

by comparing baseline simulation and simulations with selected shocks. The sensitivity of the model is evaluated by changing historical values of selected exogenous variables and periods of simulation.

Baseline Data Set and Simulation

Econometric models are often used to examine the impact of different shocks. If the model is linear than the dynamic properties can be calculated from the reduced form equations. The impact multipliers are, in fact, the coefficients of the derived reduced form equations. Alternatively, the reduced forms of linear models can be analysed as sets of stochastic difference equations and the dynamic properties can be determined¹⁸.

For the non-linear models, analytic expressions of the impact multipliers are not generally available. There is no one-to-one correspondence between the structural model and the reduced form^{19,20}. However, the multipliers can be approximated using non-linear simulation. First, a baseline simulation or simulation at mean values for the exogenous variables is computed. These baseline data are compared to simulations with the same exogenous data but including shocks for computing the multipliers, approximately.

Method for calculating multipliers. In order to calculate the multipliers, a method similar but less complete than Fair²⁰ was adopted. It is assumed that the parameters are known with certainty and all stochastic terms are eliminated. Fair used stochastic dynamic simulation while in this analysis a deterministic simulation is used. Both methods utilised a non-linear solution for the full model.

The present model which has a yearly time frame is adapted to Fair's for quarterly models. Following Fair's notation, let the *i*th equation for the model be

$$\phi i(y_{it} \dots y_{Gt}, Z_{it} \dots Z_{nt}, B_{it}) = 0$$

where y_{it} are the endogenous variables
 Z_{it} the predetermined variables
 B_{it} are the estimated coefficients.

TABLE 4. SUMMARY OF PAST STUDIES ON NATURAL RUBBER

Reference	Supply function estimated	Elasticities		Feature
		Short-run	Long-run	
Stern	Pen. Malaysia	0.4661		Supply-inventory relationship
	Estate	-0.01		
	Smallholding	0.02		
Behrman	Pen. Malaysia	0.141		Adaptive expectation model
	Estate	-0.09		
	Smallholding	0.029		
	Indonesia	0.474		
	Estate	0.054		
	Smallholding	0.333		
	Thailand	0.409		
Cheong		Static	Dynamic	1. Theory of the firm and partial adjustment model 2. Storage theory, static and extrapolative expectations 3. Price of competing crop
	Pen. Malaysia	0.057	0.1403	
	Indonesia	0.114	0.0720	
	Thailand	0.068	0.0194	
Dowling	Thailand	0.092 to 0.265	1.205 to 2.641	Vintage production function and Almon lag
Blandford	Pen. Malaysia	0.294	0.358	Theory of capital investment
	Indonesia	0.086	0.125	
	Thailand	0.644	1.452	
World Bank	Pen. Malaysia	0.22		Partial adjustment model
	Indonesia	0.18		
	Thailand	0.25		
	Rest of the world	0.19		
Tan	Pen. Malaysia			Vintage production function and Almon lag
	Estate	0.3007	8.9245	
	Smallholding	0.6865	-1.0407	
	Indonesia			
	Estate	0.4945	5.6557	
	Smallholding	0.3586	6.6673	
	Thailand	0.3952	6.7137	

There is no error term in the equation since B_i is previously estimated. The simulation is thus non-stochastic.

Let \bar{X}_1 be a particular vector of exogenous variable for the period of interest (\bar{X}_1 in this instance is the vector of mean values) and y_{it} the simulated value of the endogenous variable i in period t . Let \bar{X}_2 be a vector of the exogenous variables changed by a certain percentage, then y_{it} is the simulated value of variable i which is conditional on X_2 and β . Then the difference in value for the endogenous variable due to the change in values of the exogenous variable from \bar{X}_1 to \bar{X}_2 can be calculated by

$$\gamma_{it} = \bar{y}_{it}(\hat{\beta}_1, X_2) - y_{it}(\hat{\beta}_1, X_1) \quad \dots 55$$

Impact multiplier analysis. The method above was used to calculate the multipliers of the model. Multiplier estimates are reported in terms of percentage changes. Several experi-

ments were conducted with the baseline data as reference. First, the exogenous variables were increased by 10% from their base value and the system shocked for one year only *i.e.* 1960. Second, the increased values of the exogenous variables were maintained through the period of simulation.

The exogenous variables used in the policy simulations were the price of palm oil, *PPOIL*, and export tax, *TAX*. For the policy variable *TAX*, the prices used in *NP* and *REM* were adjusted at the means for the tax.

Tables 5 and 6 show the percentage changes in values of selected endogenous variables due to a one-time or one-period shock in the exogenous variables. *Tables 7 and 8* show the selected multiplier effects due to sustained shocks to the system. These shocks are the same as the one-period shocks but are sustained throughout the simulation period.

TABLE 5. SELECTED IMPACT MULTIPLIERS DUE TO ONE-PERIOD CHANGE IN PRICE OF PALM OIL

Year	NP ^S _t	MA ^S _t	NP ^E _t	MA ^E _t	PTOTNR	RSSINY
1960	-0.017504	0.000000	-0.001693	-0.000148	-0.000036	0.00025845
1961	-0.020099	-0.000835	-0.019827	-0.000838	-0.000337	0.00229945
1962	-0.015566	-0.000029	-0.010885	-0.000414	-0.000105	-0.00055868
1963	-0.012104	-0.000002	-0.006046	-0.000204	-0.000049	-0.00005072
1964	-0.009442	-0.000000	-0.003394	-0.000101	-0.000024	-0.00001696
1965	-0.007382	-0.000000	-0.001924	-0.000049	-0.000012	-0.00000809
1966	-0.005783	-0.000000	-0.001101	-0.000025	-0.000006	-0.00000398
1967	-0.004537	-0.000000	-0.000635	-0.000012	-0.000003	-0.00000197
1968	-0.003563	-0.000000	-0.000368	-0.000006	-0.000001	-0.00000097
1969	-0.002801	-0.000000	-0.000215	-0.000003	-0.000000	-0.00000048
1970	-0.002203	-0.000000	-0.000126	-0.000001	-0.000000	-0.00000024
1971	-0.001734	0.000000	-0.000075	-0.000000	-0.000000	-0.00000012
1972	-0.001365	0.000000	-0.000044	-0.000000	-0.000000	-0.00000005
1973	-0.001075	0.000000	-0.000026	-0.000000	-0.000000	-0.00000000
1974	-0.000847	0.000000	-0.000016	-0.000000	-0.000000	-0.00000000
1975	-0.000668	0.000000	-0.000009	-0.000000	-0.000000	-0.00000000
1976	-0.000526	0.000000	-0.000006	-0.000000	-0.000000	-0.00000000
1977	-0.000414	0.000000	-0.000003	-0.000000	-0.000000	-0.00000000
1978	-0.000327	0.000000	-0.000002	-0.000000	-0.000000	-0.00000000
1979	-0.000258	0.000000	-0.000000	-0.000000	-0.000000	-0.00000000
1980	-0.000203	0.000000	-0.000000	-0.000000	-0.000000	-0.00000000

TABLE 6. SELECTED IMPACT MULTIPLIERS DUE TO A ONE-PERIOD CHANGE IN EXPORT TAX

Year	NP^S_t	MA^S_t	NP^E_t	MA^E_t	PTOTNR	RSSINY
1960	-0.0022367	0.00000000	-0.006562	-0.00003017	-0.000007254	0.00005247
1961	-0.0029194	-0.00016963	-0.007654	-0.00017046	-0.000068376	0.00046641
1962	-0.0022611	-0.00000609	-0.004333	-0.00008418	-0.000021220	-0.00011344
1963	-0.0017588	-0.00000022	-0.002478	-0.00004157	-0.000010029	-0.00001030
1964	-0.0013715	-0.00000001	-0.001429	-0.00002053	-0.000004936	-0.00000344
1965	-0.0010724	-0.00000000	-0.000831	-0.00001014	-0.000002437	-0.00000164
1966	-0.0008401	-0.00000000	-0.000486	-0.00000501	-0.000001203	-0.00000081
1967	-0.0006590	-0.00000000	-0.000286	-0.00000247	-0.000000594	-0.00000040
1968	-0.0005176	-0.00000000	-0.000169	-0.00000122	-0.000000293	-0.00000020
1969	-0.0004069	-0.00000000	-0.000100	-0.00000060	-0.000000145	-0.00000010
1970	-0.0003200	0.00000000	-0.000059	-0.00000030	-0.000000072	-0.00000005
1971	-0.0002519	0.00000000	-0.000036	-0.00000015	-0.000000035	-0.00000002
1972	-0.0001983	0.00000000	-0.000021	-0.00000000	-0.000000000	-0.00000000
1973	-0.0001562	0.00000000	-0.000013	-0.00000000	-0.000000000	-0.00000000
1974	-0.0001230	0.00000000	-0.000008	-0.00000000	-0.000000000	-0.00000000
1975	-0.0000969	0.00000000	-0.000005	-0.00000000	-0.000000000	-0.00000000
1976	-0.0000764	0.00000000	-0.000003	-0.00000000	-0.000000000	-0.00000000
1977	-0.0000602	0.00000000	-0.000001	-0.00000000	-0.000000000	-0.00000000
1978	-0.0000475	0.00000000	-0.000000	-0.00000000	-0.000000000	-0.00000000
1979	-0.0000374	0.00000000	-0.000000	-0.00000000	-0.000000000	-0.00000000
1980	-0.0000295	0.00000000	-0.000000	-0.00000000	-0.000000000	-0.00000000

TABLE 7. SELECTED IMPACT MULTIPLIERS DUE TO A SUSTAINED INCREASE IN PRICE OF PALM OIL

Year	NP^S_t	MA^S_t	NP^E_t	MA^E_t	PTOTNR	RSSINY
1960	-0.10336	-0.000866	-0.046565	-0.0017999	-0.00057368	0.00191543
1961	-0.10334	-0.000866	-0.046363	-0.0018015	-0.00057404	0.00191581
1962	-0.10332	-0.000866	-0.046243	-0.0018023	-0.00057422	0.00191506
1963	-0.10330	-0.000866	-0.046178	-0.0018027	-0.00057431	0.00191500
1964	-0.10329	-0.000866	-0.046121	-0.0018029	-0.00057435	0.00191497
1965	-0.10328	-0.000866	-0.046093	-0.0018029	-0.00057437	0.00191496
1966	-0.10328	-0.000866	-0.046075	-0.0018030	-0.00057439	0.00191495
1967	-0.10327	-0.000866	-0.046064	-0.0018030	-0.00057439	0.00191495
1968	-0.10327	-0.000866	-0.046057	-0.0018030	-0.00057439	0.00191495
1969	-0.10326	-0.000866	-0.046053	-0.0018030	-0.00057439	0.00191495
1970	-0.10326	-0.000866	-0.046051	-0.0018030	-0.00057440	0.00191495
1971	-0.10326	-0.000866	-0.046049	-0.0018030	-0.00057440	0.00191495
1972	-0.10326	-0.000866	-0.046049	-0.0018030	-0.00057440	0.00191495
1973	-0.10326	-0.000866	-0.046048	-0.0018030	-0.00057440	0.00191495
1974	-0.10326	-0.000866	-0.046048	-0.0018030	-0.00057440	0.00191495
1975	-0.10325	-0.000866	-0.046047	-0.0018030	-0.00057440	0.00191495
1976	-0.10325	-0.000866	-0.046047	-0.0018030	-0.00057440	0.00191495
1977	-0.10325	-0.000866	-0.046047	-0.0018030	-0.00057440	0.00191495
1978	-0.10325	-0.000866	-0.046047	-0.0018030	-0.00057440	0.00191495
1979	-0.10325	-0.000866	-0.046047	-0.0018030	-0.00057440	0.00191495
1980	-0.10325	-0.000866	-0.046047	-0.0018030	-0.00057440	0.00191495

TABLE 8. SELECTED IMPACT MULTIPLIERS DUE TO A SUSTAINED INCREASE IN EXPORT TAX

Year	NP^S_t	MA^S_t	NP^E_t	MA^E_t	PTOTNR	RSSINY
1960	-0.014707	-0.00017595	-0.02455	-0.00036632	-0.00011649	0.000388541
1961	-0.014711	-0.00017595	-0.02441	-0.00036665	-0.00011656	0.000388491
1962	-0.014714	-0.00017595	-0.02433	-0.00036680	-0.00011660	0.000388467
1963	-0.014716	-0.00017595	-0.02427	-0.00036688	-0.00011661	0.000388455
1964	-0.014718	-0.00017595	-0.02424	-0.00036692	-0.00011662	0.000388449
1965	-0.014720	-0.00017595	-0.02422	-0.00036694	-0.00011663	0.000388446
1966	-0.014721	-0.00017595	-0.02421	-0.00036695	-0.00011663	0.000388445
1967	-0.014722	10.00017595	-0.02420	-0.00036696	-0.00011663	0.000388444
1968	-0.014722	-0.00017595	-0.02420	-0.00036696	-0.00011663	0.000388444
1969	-0.014723	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1970	-0.014723	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1971	-0.014723	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1972	-0.014724	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1973	-0.014724	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1974	-0.014724	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1975	-0.014724	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1976	-0.014724	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1977	-0.014724	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1978	-0.014724	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1979	-0.014724	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443
1980	-0.014724	-0.00017595	-0.02419	-0.00036696	-0.00011663	0.000388443

From *Tables 5 and 6*, as expected the multiplier effects of the one-period shock to the system tapered off over time. The supply shifters' effects on the estate sector were more pronounced and extended over a longer period than those of the smallholder sector. The impact of a tax increase was bigger for the estate sector than the smallholder sector with both sectors witnessing a negative percentage change in new plantings and mature area. Effects on total natural rubber production were greater for a change in *PPOIL* than for a change in *TAX*. The impacts of the supply shifters conform with economic theory where a short-term decrease in supply is expected to cause the price to increase immediately, reach a maximum and then decrease due to adjustments. For example, the percentage change in price due to *TAX* and *PPOIL* changes resulted in an increase in price in 1960, which reached a maximum in 1961 and thereafter the percentage change in price declined.

Sustained shock experiments were also conducted for both policy variables. The multiplier effects for the sustained shocks were larger than those for the one-year shocks. Sustained shocks for the supply shifters were accumulative over the years. The effects on production and price were larger than the one-period shock and tended to stabilise after a number of years.

In all these experiments it should be noted that the multiplier effect indicates the magnitude of impact of an exogenous variable on the endogenous variables. The simulations are conducted on a partial basis. For example, the multiplier effect for a change in *PPOIL* by 10% in one year caused new plantings in the smallholder sector to change by -0.00175% in the first year, a -0.0201% change in the second year and so forth, holding other factors constant. It is emphasised that other factors, the predetermined variables at the mean levels, were held constant.

Sensitivity analysis. To evaluate the model performance, similar policy simulations to those of the multipliers were carried out with different initial periods of simulations or in the initial conditions; the method of calculating the multiplier impacts was also the same. However, in this instance instead of using the baseline values, the actual historical data were used.

The exogenous variables selected for the examination were the same. In the first simulation the historical values were increased by 10% and simulation was initiated for 1975 - 80. In the second experiment, the historical values were decreased by 10% and the simulation conducted over the same period. Results of both simulations are shown in *Tables 9 and 10.*

TABLE 9. PERCENTAGE CHANGE IN IMPACT WITH 10% CHANGE IN PRICE OF PALM OIL

Year	NP ^S	MA ^S	NP ^E	MA ^E	PTOTNR	RSS1NY
10% increase						
1976	-0.011743	0.00000000	0.020640	-0.0003386	-0.00006210	0.00049078
1977	-0.026843	-0.00097271	-0.001174	-0.0023654	-0.00064551	0.00451524
1978	-0.041585	-0.00099788	-0.013298	-0.0034619	-0.00078781	0.00318518
1979	-0.055541	-0.00088835	-0.019329	-0.0037736	-0.00077474	0.00253277
1980	-0.066745	0.00070479	-0.021650	-0.0036203	-0.00069063	0.00197378
10% decrease						
1976	0.143522	0.00000000	-0.025227	0.0003296	0.0000615	-0.0004908
1977	0.032807	0.00097210	0.011564	0.0023654	0.0006982	-0.0045175
1978	0.050826	0.00099788	0.017113	0.0034618	0.0007878	-0.0031722
1979	0.067883	0.00088834	0.025115	0.00377356	0.0007747	-0.0025245
1980	0.081577	0.00070479	0.028355	0.00362025	0.0006906	-0.0019688

TABLE 10. PERCENTAGE CHANGE IN IMPACT WITH 10% CHANGE IN EXPORT TAX

Year	NP ^S	MA ^S	NP ^E	MA ^E	PTOTNR
10% increase					
1976	-0.001673	0.00000000	-0.009324	-0.0001036	-0.00001899
1977	-0.004758	-0.00029811	-0.025448	-0.0007650	-0.00020405
1978	-0.008010	-0.00040862	-0.035459	-0.0013216	-0.00030561
1979	-0.011743	-0.00035001	-0.046806	-0.0014918	-0.00030400
1980	-0.015252	-0.00032701	-0.058756	-0.0015616	-0.00030085
10% decrease					
1976	0.001673	0.00000000	0.009323	0.00009876	0.00001809
1977	0.004758	0.00028411	0.025458	0.00072728	0.00019415
1978	0.008010	0.00038449	0.035419	0.00124741	0.00028818
1979	0.011743	0.00032998	0.046998	0.00140622	0.00028818
1980	0.015252	0.00030578	0.059043	0.00146574	0.00028213

Several observations can be made from the simulated results. First, the impacts of the supply shifters seemed to build up from year to year. This is the reflection of the lags in the phenological structure in the model, indicating cumulative effects of investment and disinvestment decisions. Secondly, the magnitude of the effects due to a 10% increase or decrease are about the same but in the opposite direction.

Forecasting

There are two types of forecasting, *ex post* and *ex ante*. In *ex post* forecasting exogenous variables are known with certainty while in *ex ante*, the dependent variable is forecasted by using exogenous variables whose values may or may not be known. *Ex post* forecasting can be used as a means of evaluating a model by comparing the forecast values with the historical data. It is useful not only for predictive purposes but also for sensitivity and policy analysis. The *ex post* forecast is utilised in this study.

The model was used to forecast the endogenous variables for 1981 and 1982. The forecasted values obtained were compared with the actual values of the endogenous variables. Various criteria can be used in evaluating the forecasting capability of the model, namely;

- Root mean square error
- Root mean square per cent error
- Mean percent error
- Theil inequality coefficient.

For Theil's inequality coefficient, if $U = 0$, the forecasted value is equal to the actual value and if $U = 1$, the opposite holds²¹. The endogenous variables MA^S_t , $PRODUCTION^S_t$, REM^S_t , MA^E_t performed better than others with U coefficient values falling between 0.011 and 0.046. The poorest forecasting performance was for NP^E_t . Table 11 shows the forecasted and actual values of the endogenous variables, while Table 12 shows the values obtained for the various statistical criteria used in evaluating the forecasting performance of the model.

CONCLUSION

The objective of the paper was to illustrate an alternative approach to estimating supply response of a perennial crop by incorporating the phenological structure. The incorporation of such *a priori* information provides useful information in the formulation of lags in the dynamic supply functions. Results obtained from the analysis showed that the incorporation captured explicitly the dynamic property of the production process thus reflecting the structural integrity of the model.

The value of incorporating the phenological process for the trees together with an adequate economic structure has wider implications for policy analysis as reflected in the results obtained from the policy simulation exercises. The effects of a one-time and sustained shocks conform with economic theory. The multiplier effects of a one-time shock to the system tapered off over time while sustained shocks

TABLE 11. FORECAST AND ACTUAL VALUES OF ENDOGENOUS VARIABLES 1981 AND 1982

Variable	1981		1982	
	Actual	Forecast	Actual	Forecast
REM^E_t	12.80000	19.8884	6.40000	19.524100
NP^E_t	38.00000	28.2707	37.80000	37.641000
δ^E_t	0.71875	0.7293	0.91416	0.814632
MA^E_t	926.90000	914.5560	943.80000	926.849000
$PRODUCTION^E$	882.30000	870.5500	902.30000	886.095000
REM^S_t	20.00000	26.6822	22.50000	22.202500
δ^S_t	3.81551	0.5461	3.74242	1.396660
MA^S_t	416.70000	405.8260	403.90000	401.251000
$PRODUCTION^S$	574.30000	585.7400	576.70000	596.700000

TABLE 12. STATISTICAL CRITERIA FOR EVALUATING FORECASTING CAPABILITY OF MODEL

Variable	Mean error	Mean percent error	Root mean square	Theil U
REM ^E _t	10.106	1.302	14.292	0.479
NP ^E _t	-5.159	-0.127	7.297	0.219
δ ^E _t	0.005	0.128	1.414	0.646
MA ^E _t	-14.678	-0.016	20.715	0.011
PRODUCTION ^E _t	-13.978	-0.016	19.767	0.011
REM ^S _t	3.192	0.174	4.515	0.098
NP ^S _t	4.549	4.136	6.434	0.325
δ ^S _t	-2.808	-0.742	3.970	0.257
MA ^S _t	-6.7613	-0.016	9.562	0.012
PRODUCTION ^S _t	-133.506	0.239	188.806	0.162

for the supply shifters were accumulative over the years. Results from the sensitivity analysis add credence, as the impact of the supply shifters seemed to build up from year to year — a reflection of the lags in the phenological structure of the model, indicating cumulative effects of investment and disinvestment decision.

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Impedance of Latex Exudation by the Bark Excision Wound During Tapping

H.Y. YEANG*

The surfaces of the tapping cuts on Tjir 1 and RRIM 623 trees were scraped immediately after tapping to enhance wounding arising from excision of the bark shavings. A marked increase in the rate of latex vessel plugging and a decrease in yield were observed, suggesting that wounding the surface of the tapping cut contributed towards latex vessel plugging. Re-tapping GT 1 and RRIM 501 trees 80 min after the initial tapping, before flow from the initial tapping had ceased, extended the flow duration. However, GT 1 trees that were re-tapped 20 min after the initial tapping did not show an increase in flow duration. In fact, a significant decrease was observed in RRIM 501 trees that were similarly treated. This suggests that wounding arising from bark excision during tapping has a significant role in latex vessel plugging and the restriction of latex outflow. Impedance of latex flow is possibly mediated through destabilisation of latex by coagulants released by the injured bark tissue.

When the rubber tree is tapped, the high turgor pressure built up within the laticifer system expels its contents: hence the exudation of latex. While the diminution of latex flow rate during the course of flow may be partly explained by the decrease in turgor, another mechanism also intervenes to impede latex loss from the tapped vessels. This mechanism, termed latex vessel plugging, seals off the exuding vessels at or very near their cut ends. Several modes of action have been proposed to explain latex vessel plugging¹. In particular, emphasis has been placed upon the destabilisation of latex at the tapping cut induced by the damage to lutoids (a vesicular component of latex) when they are subjected to various physical stresses as the latex emerges from the laticifers. Bark exudate or bark sap that is released when the tree is tapped has also been suggested as a precipitant of plugs^{2,3} although this suggestion has not received as much attention. In this instance, the resultant plugging might be regarded as a response to bark wounding. The proposition has been supported by observations in the laboratory that *Hevea* bark extract destabilises diluted fresh latex or a suspension of rubber particles^{2,3,4}. Nevertheless, doubt has been raised as to whether coagulants released by

tapping could diffuse back into the vessels to effect plugging, especially during the initial rapid flow although this is plausible near the cessation of flow⁵. Southorn⁵ noted, for example, that the flow of fresh latex through narrow bore glass capillaries was not stopped when their ends were immersed into coagulating solutions such as formic acid. Gomez² opined that bark juice from cells damaged by the tapping knife flocculated latex to form a network on the surface of the tapping cut; latex particles were subsequently entrapped in this network. Essentially, the uncertainty in respect of the role of bark sap in latex vessel plugging stems from the extrapolation of unresolved laboratory findings to the situation in the field. To date, neither bark wounding nor bark sap has been shown to induce latex vessel plugging *per se* or to impede latex outflow from trees in the field.

This paper describes a study which demonstrates in the field the impedance of latex exudation as a response to the wounding of bark tissue at the tapping cut. It should be made clear from the outset that 'wounding' in the context of this paper refers to the wounding of the bark at the surface of a normal tapping cut

*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

and not, as in popular use, wounding of the cambium as a result of over-deep tapping.

MATERIALS AND METHODS

Effect of Scraping the Tapping Cut

Eighteen trees each of RRIM 623 and Tjir 1, tapped $\frac{1}{2}$ S d/2 on *Panel BI-1*, were selected on the basis of similarity in girth, yield and plugging index. To attain closer matching between control and treated trees, the selected trees were then paired and one tree of each pair was assigned as a 'control' tree and the other a 'treatment' tree. Immediately after excision of the bark shavings of 'treatment' trees when they were tapped, the surfaces of the tapping cuts were scraped with a segment of a hacksaw blade (eight 'teeth' per centimetre) to augment wounding resulting from the tapping operation. Scraping was carried out only on *alternate* tapping days (designated 'treatment' days); on non-'treatment' days, scraping was not carried out after tapping. In control trees, scraping was not carried out at all, either on 'treatment' or non-'treatment' days.

The initial rate of flow was calculated by collecting the first half minute flow into a pre-weighed vial and re-weighing.

To calculate the intensity of plugging^{6,7} at the 20th min (IP_{20}), the trees were re-tapped 20 min after the initial tapping (before latex flow had ceased). IP was calculated as:

$$\frac{\text{Wt. of latex exuded } \frac{1}{2} \text{ min after re-tapping} - \text{Wt. of latex exuded } \frac{1}{2} \text{ min before re-tapping}}{\text{Wt. of latex exuded } \frac{1}{2} \text{ min after re-tapping}} \times 100$$

IP values were transformed into angles for computation and back-transformed for result presentation. As IP measurements required the trees to be re-tapped 20 min after the initial tapping, IP readings and yield readings were not taken on the same days.

Bursting index of lutoids was determined based on the method of Ribailleur⁸. The first 30 min flow of latex after tapping

was collected in chilled containers and centrifuged for 1 h in a Sorvall RC-2B centrifuge at 19 000 r.p.m. (44 000 g max) at temperatures between 3°C and 4°C. The latex separated into three main fractions: an upper rubber phase, a 'bottom fraction' comprising largely of lutoids and a middle liquid phase (C serum). Acid phosphatase activity in C serum (termed 'free' acid phosphatase) was determined by the change in optical density at 400 nm using p-nitrophenylphosphate as the substrate, the reaction being carried out in 0.1M citrate buffer, pH 5. Another sample of the same latex was diluted with Triton X-100 (1 part latex: 4 parts 0.125% Triton X-100) to rupture the vesicular components of the latex. The mixture was centrifuged as before and the liquid phase obtained after centrifugation comprised essentially of a mixture of C serum and B serum (released from ruptured lutoids) together with the Triton X diluent. 'Total' acid phosphatase of latex was estimated from the enzyme activity in the liquid phase so obtained. As latex acid phosphatase is essentially confined to the lutoids when they are intact, the ratio of 'free' to 'total' acid phosphatase represents the 'bursting index' of lutoids. (See *Appendix A* for details of the calculation of the bursting index.)

For light microscopy, bark discs were sampled just below the tapping cut using a metal punch and were fixed in formalin-acetic acid-alcohol (FAA). Radial longitudinal sections (to count the number of latex vessel rings) and tangential longitudinal sections (to count the number of latex vessels per unit length of each ring) were prepared, stained in Sudan III and mounted in glycerine jelly.

Effect of Re-tapping at Varying Intervals

Four trees each of GT 1 and RRIM 501, tapped $\frac{1}{2}$ S d/2 on *Panel BI-1*, were selected on the basis of closely matching yield, girth and plugging index. The rate of flow of each tree was monitored by volume measurements taken at 5 min intervals. Thus, the number of trees used in this experiment was necessarily limited by the detailed measurements being made on each individual tree. A 'change-over' design based on a 4 × 4 Latin Square as described by

Cochran *et al.*⁹ and Patterson¹⁰ was adopted for the experiment. The trees were subjected to four treatments:

- Control (not re-tapped)
- Re-tapped at the 20th min from the time of the initial tapping
- Re-tapped at the 50th min
- Re-tapped at the 80th min.

On a 'treatment' day, the four trees of each clone were each subjected to one of the four treatments. On subsequent 'treatment' days, the four treatments were rotated sequentially among the trees. On completion of one cycle, therefore, each of the four trees would have been subjected once to each treatment. Two cycles were completed for each of the two clones. This experimental design was considered particularly suited to the experiment as it suppressed the errors arising from tree-to-tree variation normally associated with experiments having small numbers of trees. The principal effects of tree-to-tree variation were largely eliminated as each tree was subjected to each one of the four treatments. At the same time, the principal effects of day-to-day variation were largely eliminated as all four treatments were carried out on each of the 'treatment' days.

Treatments were carried out only on alternate tapping days to minimise 'carry-over' effects from one treatment to another. Nevertheless, it was still necessary to check if such effects were present. As the treatments were carried out on alternate tapping days (*i.e.* once every two tapping days), yield and initial flow rate of another two sets of trees (GT 1 and RRIM 501 of the same population as the experimental trees) were measured two tapping days after they had been subjected to re-tapping at the 80th min — which was the most severe treatment — on three preceding alternate tapping days. The treated trees showed a discrepancy of an order of only 5% in yield and initial flow rate when compared to control trees that were not re-tapped (based on replicated readings of eighteen paired treated and control trees of each clone). Thus, it could be assumed that 'carry-over' effects between treatments on latex flow were negligible in the short term.

RESULTS AND DISCUSSION

Effect of Scraping the Tapping Cut

Scraping the surface of the tapping cut markedly increased the rate of plugging of latex vessels as indicated by IP_{20} . Within 20 min from the time of tapping, over 90% of the latex vessels were estimated to have stopped yielding in RRIM 623 and Tjir 1 trees where the tapping cuts were scraped (*Figure 1*). In control trees, plugging had occurred in less than 60% of the vessels over the same period. This difference was even more distinct when viewed in terms of the proportion of latex vessels still yielding 20 min from tapping. Thus, only about 8% of the latex vessels originally severed during tapping were still yielding in trees in which the tapping cuts were scraped as compared with 42% in control trees. On days when neither 'treatment' nor 'control' trees were scraped (non-'treatment' days), IP in both sets of trees were similar (*Figure 1*). This indicates that the effects of the treatment (in relation to plugging) were localised and that they produced no residual effects that were sustained till the next tapping day.

The greater propensity to plugging in treated trees was reflected in the rate of latex flow 20 min from the time of tapping. In both clones, the flow rates were markedly reduced in the treated trees compared with controls (*Table 1*). The effect of increased plugging was also observed in the yields of treated and control trees (*Table 1*).

The enhancement of latex vessel plugging when the tapping cut of the tree was scraped could be regarded as a response to increased wounding over that resulting from tapping alone. The exact mechanism of such wound-induced plugging is not revealed by the experiment but the results suggest that a latex destabiliser/coagulant could be released from wounded bark. When the tree is just tapped, the very rapid initial flow of latex would wash away much of the coagulant as well as flocs of destabilised latex from the cut ends of the latex vessels at the surface of the tapping cut. As the flow rate decreases, however, the flocs are not as readily swept away and latex vessel plugging

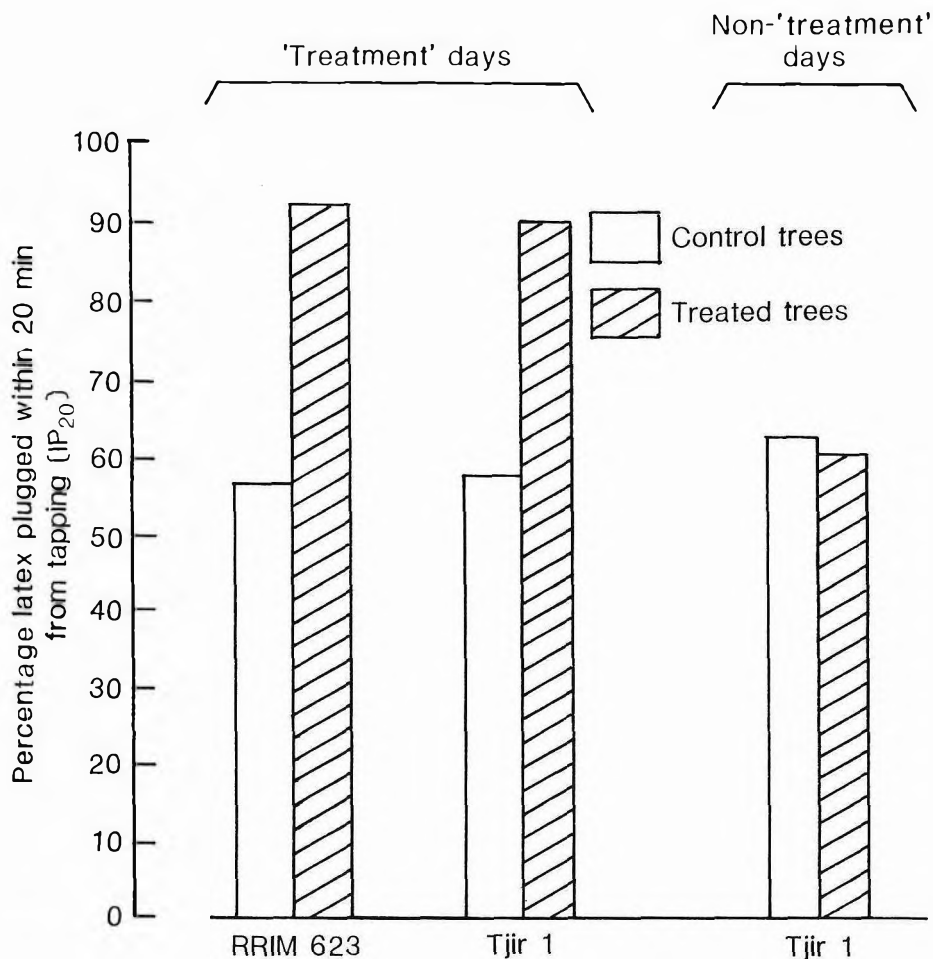


Figure 1. Effect of scraping the surface of the tapping cut on latex vessel plugging. Treated trees were scraped on 'treatment' days but not on non-'treatment' days. Values are the means of 27 readings (9 trees \times 3 replicates). Differences between control and treated trees are significant ($P < 0.001$, using the 't' test for paired samples) for 'treatment' days and not significant for non-'treatment' days. (Readings for RRIM 623 not taken on non-'treatment' days.)

TABLE 1. EFFECT OF SCRAPING SURFACE OF TAPPING CUT ON INITIAL FLOW RATE, FLOW RATE AT THE 20TH MIN AND YIELD

Tapping cut	Initial flow rate ^a (g min ⁻¹)		Flow rate at the 20th min (g min ⁻¹)		Yield (ml)	
	RRIM 623	Tjir 1	RRIM 623	Tjir 1	RRIM 623	Tjir 1
Control	12.3	10.0	2.2	1.1	93	86
Tapping cut scraped	9.0	10.4	0.7	0.5	51	71
	$P < 0.01$	N.S.	$P < 0.001$	$P < 0.05$	$P < 0.01$	$P < 0.1$

Values are the means of 27 readings (9 trees \times 3 replicates).

The levels of significance of the differences between treated and control values are indicated.

N.S. = Not significant
(Paired samples t-test)

^aFlow rate over the first $\frac{1}{2}$ min from the time of tapping

sets in. The putative coagulant need not necessarily have to back-diffuse into the latex vessels to effect plugging. Its entry into the latex vessels is possibly lateral, arising from the adjacent tissues immediately below the surface of the tapping cut where the vessel turgor pressure gradient is the greatest.

In the trees where wounding had been augmented by scraping the surface of the tapping cut, plugging was accordingly hastened. It might be argued that the apparent increase in latex vessel plugging might have arisen from deposits of fine debris from scraping the cut clogging the cut ends of the latex vessels. This seemed improbable, given the initial high turgor pressure (*circa* 10 MPa) of the laticifer system¹¹ instrumental in latex outflow. In Tjir 1 at least, the initial flow rates were similar in control and treated trees (*Table 1*) indicating that mechanical blockage had not occurred. The initial flow rate of treated RRIM 623 trees showed a significant decrease which could be attributed to the strong wound-induced latex destabilising action that persisted even in the rapid initial flow immediately after tapping. Why was this effect not observed in Tjir 1 where the initial flow rate of 10 g per millilitre was seemingly lower than the 12.3 g per millilitre of RRIM 623 control trees? The reason was that these values referred to latex flow from the entire tapping cut. The Tjir 1 trees were slightly smaller in girth than the RRIM 623 trees and so had shorter tapping cuts. More important, latex vessel density in RRIM 623 bark was far higher than in Tjir 1. As a result, the initial latex flow from the tapping cuts of RRIM 623 trees were derived from some three times as many latex vessels as those of Tjir 1 trees (*Table 2*). When the initial flow rate was expressed as the rate per latex vessel cut, it was evident that latex was being exuded from Tjir 1 latex vessels two and a half times as fast as from RRIM 623 latex vessels (*Table 2*). Hence, it would not be surprising if the putative latex coagulant resulting from scraping the cut (together with incipient plugs) was effectively washed away from the immediate vicinity of the cut ends of the latex vessels by the rapid initial latex outflow in Tjir 1, but to a lesser extent in RRIM 623.

TABLE 2. INITIAL LATEX FLOW RATE IN RELATION TO NUMBER OF LATEX VESSELS SEVERED DURING TAPPING

Clone	Latex vessels severed during tapping ^a	Initial flow rate per severed latex vessel ^b ($\mu\text{g min}^{-1}$)
RRIM 623	276 740	44.5
Tjir 1	89 640	111.6

^a Estimates exclude latex vessels within 1 mm of the cambium; these vessels are not normally cut during tapping. Bark from 9 trees of each clone was sampled.

^b Calculated from flow rate of latex exuded from the entire cut in control trees over the first ½ min from the time of tapping, as presented in *Table 1*.

As mentioned earlier, the release of latex destabilisers from damaged lutoids is generally considered a major factor leading to the onset of plugging. For example, a greater extent of lutoid damage as indicated by a rise in its bursting index has been found to be correlated with increased latex vessel plugging in RRIM 623¹². A comparison of bursting indices of lutoids in latices from treated and control Tjir 1 trees could therefore give further indications as to the nature of the increased propensity to plugging in the former. No significant difference was observed in the bursting index of lutoids between latices derived from tapping cuts that had been scraped and their controls (*Table 3*). This pointed to the existence of an alternative plugging mechanism that operated independently of lutoid damage — probably the action of a coagulant released from the wounded bark.

TABLE 3. BURSTING INDEX OF LUTOIDS IN LATEX FROM TJIR 1 TREES

Latex from	Bursting index	
	'Treatment' days	Non-'treatment' days
Control	29.5 ± 2.7	28.5 ± 2.0
Tapping cut scraped	32.0 ± 1.6	28.5 ± 1.6

Means ± standard errors based on 9 trees per treatment.

There were no significant differences between control and treated trees either on 'treatment' or non-'treatment' days.

Effect of Re-tapping at Varying Intervals

Trees were re-tapped 20 min, 50 min or 80 min after the initial tapping, before latex flow from the initial tapping had ceased. As noted by Boatman¹³, resurgence of flow was observed immediately following re-tapping as a result of the removal of plugs from the cut ends of the latex vessels. Based on the relative flow rates immediately before and immediately after re-tapping, the intensity of plugging^{6,7} was calculated, this reflecting the proportion of vessels that were plugged at the time of re-tapping. Approximately 21%, 60% and 85% of the latex vessels at the tapping cut in GT 1 and RRIM 501 were estimated to be plugged after 20 min, 50 min and 80 min respectively and these vessels were thus non-yielding by then (Table 4).

The flow duration and yield (cumulative from the initial tapping) were considerably increased (with respect to unre-tapped controls) in both clones when the trees were re-tapped at the 80th min (Table 4, Figure 2). This was to be expected as some 85% of the vessels at the tapping cut that had plugged were being re-opened by the re-tapping. For the same reason, there was a similar extension of flow duration and an increase in yield (of a lesser magnitude) when the trees were re-tapped at the 50th min. When re-tapping was brought forward to the 20th min in GT 1 trees, however,

there was no significant increase in either yield or flow duration despite the fact that the re-tapping enabled a resumption of latex exudation from the 21% of the latex vessels that had plugged (Table 4, Figure 2). When RRIM 501 was treated similarly, not only was there not any increase in yield or flow duration, but the two readings were actually *reduced*, the latter significantly ($P < 0.05$).

It is proposed that the absence of increase in yield and flow duration in GT 1 and the diminution of these measurements in RRIM 501 were effects of wounding of the bark tissue at the tapping cut arising from tapping, these effects being more marked in RRIM 501. By this argument, there are two antagonistic mechanisms influencing latex flow following re-tapping of the tree. Firstly, re-tapping re-opens latex vessels that are plugged and this tends to augment flow time and yield. Secondly, wounding of the bark that re-tapping entails causes a latex destabiliser/coagulant to be released from the wounded tissue. This has the effect of increasing latex vessel plugging and thereby inhibiting latex outflow. When the trees were re-tapped at the 80th min and 50th min in the experiment, the proportion of latex vessels that was re-opened was large; the resultant additional latex flow from the re-opened vessels was hence considerable. The flow immediately after re-tapping was relatively

TABLE 4. EFFECT OF RE-TAPPING AT VARIOUS INTERVALS ON YIELD AND FLOW DURATION

Treatment	GT 1			RRIM 501		
	Latex vessels re-opened by re-tapping ^a (%)	Yield (ml)	Flow duration (min)	Latex vessels re-opened by re-tapping ^a (%)	Yield (ml)	Flow duration (min)
Control (not re-tapped)	—	43x	123x	—	87x	146x
Re-tapped at the 20th min	21	46x	128x	21	79x	118y
Re-tapped at the 50th min	66	56xy	141xy	54	99xy	145x
Re-tapped at the 80th min	86	62y	161y	84	110y	183z

^a As represented by the intensity of plugging values at the time of re-tapping.

Values in a column bearing the same letter are not significantly different (Duncan's Multiple Range Test, $P < 0.05$).

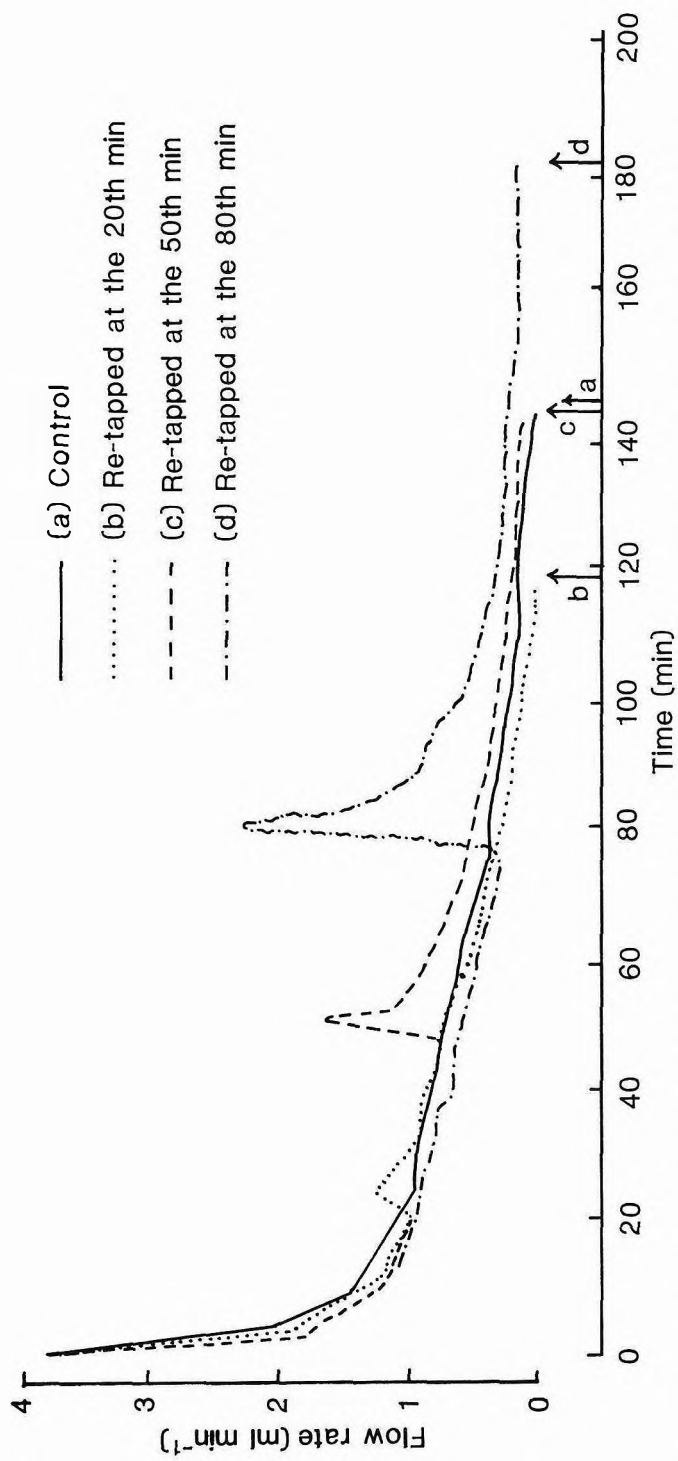


Figure 2. Effect of re-tapping RRIM 501 at various intervals on the latex flow pattern. Cessation of flow for each treatment is indicated by arrows.

rapid (*Figure 2*) and this had the effect of sweeping away the latex coagulants released by the wounded bark besides the flocs of destabilised latex (incipient plugs) from the vicinity of the cut ends of the latex vessels. Consequently, flow duration and yield increased. When the trees were re-tapped at the 20th min, on the other hand, most of the latex vessels were still yielding and the proportion of vessels that were re-opened (21%) was much smaller than in the other two re-tapping treatments. Moreover, wound-derived latex coagulants and incipient latex vessel plugs at the tapping cut could not be efficiently removed by the relatively slow rate of flow immediately after re-tapping (*Figure 2*). The net effect was that whatever gain there was in latex exudation from the re-opened vessels in GT 1 was nullified by the effect of wounding when the trees were re-tapped. In RRIM 501, the wound reaction was even stronger resulting in an overall decrease, rather than increase, in flow duration and yield.

Results from the above studies suggest that a wound reaction of the bark tissue at the tapping cut contributes significantly to latex vessel plugging. While luitoid damage remains a major factor in the overall context of plugging, it is probably not an essential feature in the alternative mechanism of wound-induced plugging described in this paper. Instead, a latex destabiliser/coagulant released by the wounded tissue might, directly or indirectly, sensitise the rubber particles to coagulation.

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APPENDIX A

DETERMINATION OF CONCENTRATION OF A SOLUTE IN WHOLE LATEX AND
CALCULATION OF BURSTING INDEX

In determining the content of a soluble constituent (e.g. a sugar, enzyme, *etc.*) of latex, it is difficult to assay whole latex as its opacity would interfere with the commonly used colorimetric methods. Frequently, the assay is carried out on the C serum which is the aqueous phase obtained after high-speed centrifugation of the latex. Although C serum is the major aqueous component of latex, its constituents may not necessarily be representative of those of latex as a whole, especially in instances where particular solutes may be localised in the various vesicular bodies (lutoids, Frey-Wyssling complexes and other minor organelles) present in latex. When latex is treated with the surfactant Triton X-100, the membranes of these vesicular bodies are ruptured and their contents are released. The combined latex serum, comprising sera derived from these vesicles together with C serum, forms an aqueous mixture with the Triton X that has been added. This mixture, when separated out by high-speed centrifugation, would be more representative of whole latex than is C serum.

After determining the concentration of the solute of interest in the combined serum-Triton X mixture, an adjustment has to be made for the dilution by Triton X so as to obtain the concentration of the solute in the undiluted combined serum or in whole latex. Consider the case where one part of latex is diluted with four parts of 0.125% Triton X. While the dilution of the uncentrifuged *whole latex* by Triton X is predetermined (1/5 in this study), the extent of dilution of the *combined serum* after centrifugal separation (and in exclusion of) the rubber and other latex solids would vary according to the relative proportions

of serum and latex solids initially present in the latex. Therefore, the adjustment for dilution by the Triton X added must take into account the insoluble solids content of the undiluted latex (the percentage total solids is an acceptable estimate). If the total solids content of the latex were, say, $s\%$, the combined serum in 100 ml of undiluted latex would be approximately $(100 - s)$ ml. When the latex is diluted 1 : 4 with Triton X, 400 ml of Triton X is added to $(100 - s)$ ml combined serum, giving a total volume of $400 + (100 - s)$ ml, *i.e.* $(500 - s)$ ml of the combined serum-Triton X mixture. To express the solute content in a sample of this mixture as its concentration in the undiluted *combined serum*, a multiplication factor of $\frac{(500 - s)}{(100 - s)}$ is applied to the solute concentration (amount per millilitre) in the serum-Triton X mixture, where s is the percentage total solids. To express the solute content as a proportion of the undiluted *whole latex*, a multiplication factor of $\frac{(500 - s)}{100}$ is applied.

In calculating the bursting index of lutoids, acid phosphatase activity in C serum is expressed as a percentage of the 'total' activity, the latter being the activity in the combined serum-Triton X mixture, after correcting for the dilution by Triton X. Thus, the bursting index is given by

$$\frac{(\text{Acid phosphatase activity in C serum})}{(\text{Acid phosphatase activity in the serum-Triton X mixture})} \times 100 \times \frac{(500 - s)}{(100 - s)}$$

where s = percentage total solids of the latex sample.

Laboratory Screening of Fungicides Using Cellulose Film and Leaf Discs Against South American Leaf Blight Pathogen, *Microcyclus ulei*

K.H. CHEE*, T.W. DARMONO** AND A.F. DOS SANTOS***

Cellulose film coated with fungicide was found to be a suitable replacement for agar medium in laboratory screening of fungicides against Microcyclus ulei. It revealed the fungicidal, fungistatic and residue effect of the chemical examined. Discs of young Hevea leaves sprayed with a fungicide and inoculated with conidia also gave a good estimate of the effectiveness and curative property of the fungicides. The effectiveness and properties of chlorothalonil, mancozeb, tridemorph, dithianon, benomyl, triforine, triadimefon, carbendazim and thiophanate methyl as they relate to South American leaf blight control were compared.

Testing of chemicals *in vitro* against phytopathogenic fungi by measuring the inhibition of mycelial growth and/or spore germination is a common technique for establishing their likely fungicidal or fungistatic effects.

The obligate nature of *Microcyclus ulei* (P. Henn.) Arx., the causal fungus of South American leaf blight (SALB) of *Hevea* rubber, permits only fungicidal tests using field conidia. Most fungicides are formulated as wettable powders, which are not readily distributed in an agar medium, although this difficulty can be partly overcome by first dissolving the fungicide in acetone before mixing it with the molten agar¹. This paper describes a technique using cellulose film instead of agar to test the fungicidal and fungistatic properties of fungicides as well as their residue effect. The method was adopted from that of Neely² who used cellophane as a medium to transfer fungicides from discs of filter paper or leaf for bioassay purposes. The use of leaf discs for laboratory fungicide tests is described. The study also attempts to compare the effectiveness and properties of the fungicides currently recommended for SALB control.

MATERIALS AND METHOD

Squares (2 × 2 cm) of cellulose film (Du Pont) were dipped in aqueous fungicide solutions at 1, 10 and 100 mg per litre for 5 s and two pieces were transferred to microscope slides. The slides were placed in open petri dishes to allow the film to evaporate off the free water. Conidia of *M. ulei* were deposited on the film by either tapping fresh leaf lesions or by transferring with a camel hair brush the desiccated conidia collected in a tapered centrifuge tube by a cyclone spore collector. The lids of the petri dishes were lined with wet filter paper and replaced to obtain 100% relative humidity. The cellulose film was incubated in the petri dish overnight before it was stained and fixed by a drop of lactophenol cotton blue. A cover slip was placed over the film. Conidia with germ tubes as long as the length of the spore were considered as having germinated. The rate of germination was expressed as a percentage of that of a fungicide-free control. The test was duplicated. The number of conidia per low-power microscope field was twenty to forty, and ten fields were counted from each film.

*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

**National Centre for Rubber Research, Sungei Putih, P.O. Box 406, Medan, Indonesia

***Convenio CEPLAC/EMBRAPA, Itabuna, Bahia, Brazil

To test for fungistatic effect, the fungicide-impregnated film carrying the conidia was incubated for 8 - 14 h and the germination counted as before. The film was floated on distilled water for a further 8 h with occasional agitation to allow the chemical on the film to be washed off and germination counted again.

To test the residue effect of the fungicide, the coated film was left in the petri dish by the window and subjected to normal changes of atmospheric conditions for various times before deposition of conidia for germination tests. In parallel tests in agar medium, the fungicide was mixed with water agar and conidial germination was counted 6 - 8 h after dry deposition of conidia. In tests with leaf discs, seven-day-old leaves of susceptible clones were used. Leaf discs (15 mm diameter) were placed inside the lids of petri dishes, with the abaxial surface uppermost and sprayed with a suspension of the test fungicide. After being allowed to dry, they were floated on distilled water, with the abaxial surface uppermost, in the lower half of the same petri dish. The discs were sprayed with a conidial suspension³. To test the curative property of the chemicals, the inoculated leaf discs were sprayed with the test fungicides on the same day and after one, two and three days' incubation. The plates were incubated under continuous light (2600 lux) at 24°C for six days and the

number and size of lesions recorded. The fungicides tested are given in *Table 1*.

RESULTS AND DISCUSSION

The cellulose film method of testing fungicides gave similar results to those of the agar plate method (*Table 2*). The germination of conidia of *M. ulei* was completely inhibited by a concentration of 100 mg per litre of chlorothalonil, mancozeb, tridemorph, dithianon, benomyl and triforine, but not by the same concentration of triadimefon, carbendazim and thiophanate methyl. Treatments which allowed germination to increase after fungicide was washed off from the film by floating on water were dithianon, benomyl, triadimefon, carbendazim and thiophanate methyl. These fungicides may therefore be regarded as weakly fungicidal but strongly fungistatic. Fungicides which continued to inhibit the germination at 100 mg per litre after the film was floated on water were chlorothalonil, mancozeb, tridemorph and triforine. These compounds are therefore strongly fungicidal to *M. ulei* at this concentration (*Table 3*). Chlorothalonil has the strongest residue effect followed by tridemorph, mancozeb, triforine, dithianon and benomyl (*Table 4*). Germination of fresh conidia on fungicide-free film was over 90%

TABLE 1. FUNGICIDES TESTED AGAINST *M. ULEI*

Type	Common/ chemical name	Concentration of active ingredient in formulation		Trade name
		Wettable powder (g/kg)	Liquids (g/litre)	
Systemic	Triadimefon	250		Bayleton
	Benomyl	500		Benlate
	Thiophanate methyl	500		Cercobin
	Carbendazim	500		Delsene
	Tridemorph		750	Calixin
	Triforine		190	Saprol
	Non-systemic	Chlorothalonil	750	
Dithianon		750		Delan
Mancozeb		980		Dithane M45

TABLE 2. GERMINATION OF CONIDIA OF *M. ULEI* ON AGAR AND CELLULOSE FILM COATED WITH FUNGICIDES

Fungicide	Concentration (mg a.i./litre)	Germination (%)	
		Agar	Cellulose film
Chlorothalonil	100	0	0
	10	0	0
	1	0	0
Mancozeb	100	0	0
	10	0	4
	1	0	23
Tridemorph	100	0	0
	10	5	12
	1	94	93
Dithianon	100	0	0
	10	5	10
	1	91	81
Benomyl	100	0	0
	10	26	23
	1	45	47
Triforine	100	0	0
	10	24	29
	1	74	77
Triadimefon	100	11	13
	10	51	42
	1	57	61
Carbendazim	100	31	37
	10	49	53
	1	55	64
Thiophanate methyl	100	37	46
	10	72	73
	1	91	93

F = 0.0693

$F_{0.1}(1/52) = 2.81$

TABLE 3. GERMINATION OF CONIDIA OF *M. ULEI* ON FUNGICIDE-COATED CELLULOSE FILM BEFORE AND AFTER FLOATING THE FILM ON WATER

Fungicide	Concentration (mg a.i./litre)	Germination (%)	
		Before floating film on water	After floating film on water for 48 h
Chlorothalonil	100	0	0
	10	0	0
	1	0	0
Mancozeb	100	0	0
	10	4	6
Tridemorph	100	0	0
	10	12	18
Dithianon	100	0	27
Benomyl	100	0	42
Triforine	100	0	2
	10	29	31
Triadimefon	100	13	69
Carbendazim	100	37	75
Thiophanate methyl	100	46	63

L.S.D._{0.05} = 11.07

and that of desiccated conidia not less than 60%.

In tests using leaf discs, the number of lesions^{3,4} rather than their size gave a good indication of the effectiveness of the fungicides.

The number of lesions formed on the discs ranged from zero to twenty-five or more depending on the fungicide and its concentration (*Table 5*). The slight variation in results in *Tables 2* and *5* was probably caused by the different effects of fungicides on physiologic

TABLE 4. PERSISTENCE OF FUNGICIDES ON CELLULOSE FILM TESTED AGAINST *M. ULEI* — GERMINATION OF CONIDIA TREATED ZERO, THREE AND SIX DAYS EARLIER WITH FUNGICIDES

Fungicide	Concentration (mg a.i./litre)	Germination (%)		
		0 day	3 days	6 days
Chlorothalonil	100	0	0	0
	10	0	0	0
	1	0	0	8
Mancozeb	100	0	0	16
	10	4	29	63
Tridemorph	100	0	0	0
	10	12	17	42
Dithianon	100	0	11	35
Benomyl	100	0	53	65
Triforine	100	0	5	8
Triadimefon	100	13	75	79
Carbendazim	100	37	38	43
Thiophanate methyl	100	46	46	48

TABLE 5. EFFECT OF FUNGICIDES ON NUMBER AND SIZE OF LESIONS ON HEVEA LEAF DISCS FOLLOWING INOCULATION WITH CONIDIA OF *M. ULEI*

Fungicide	Concentration (mg a.i./litre)	Average number of lesions/leaf disc (15 mm diameter)	Average lesion size (μm)
Chlorothalonil	1	0	—
Mancozeb	50	0	—
Triadimefon	50	0	—
Triforine	50	0	—
Tridemorph	100	0	—
Tridemorph	50	1	433
Benomyl	100	3.1	310
Triforine	10	4.4	433
Triadimefon	10	9.8	237
Benomyl	50	12.7	307
Thiophanate methyl	100	16.7	350
Mancozeb	10	17.4	433
Dithianon	100	19.2	420
Carbendazim	100	21.9	427
Dithianon	50	23.6	430
Carbendazim	50	24.6	430
Thiophanate methyl	50	27.8	357
Control	—	37.1	430
		L.S.D. _{0.05} = 4.4	L.S.D. _{0.05} = 43.9
		H.S.D. _{0.01} = 8.8	

TABLE 6. DIFFERENCES IN LESION FORMATION ON LEAF DISCS SEVEN DAYS AFTER INOCULATION WITH *M. ULEI* AND APPLICATION OF FUNGICIDES ON THE FIRST, SECOND AND THIRD DAYS

Fungicide, 100 mg/litre	Lesion formation, transformed values $\sqrt{x + \frac{1}{2}}$			
	1st day	2nd day	3rd day	Mean
Triadimefon	0.71(0)	0.88(0)	2.30(5)	1.30
Benomyl	0.71(0)	3.03(9)	4.09(17)	2.61
Chlorothalonil	0.71(0)	1.79(3)	3.52(12)	2.01
Mancozeb	0.71(0)	2.80(8)	4.22(18)	2.58
Mean	0.71	2.13	3.53	
		L.S.D. = 0.59		
				L.S.D. = 0.64

Figures within brackets are the actual numbers of lesions.

ances of *M. ulei*⁴. Fungicides currently recommended⁵ for the control of SALB are chlorothalonil, mancozeb, triadimefon and benomyl, all of which prevented lesion formation at concentrations up to 100 mg per litre. Chlorothalonil at 1 ml per litre gave the same result as mancozeb and triadimefon at 50 mg per litre and benomyl at 100 mg per litre. Among the four recommended fungicides, chlorothalonil appeared to be the best because it was effective at very low concentrations, had residue effect and was both fungicidal and fungistatic. Nursery trials had confirmed chlorothalonil to be one of the most effective fungicides against SALB⁶. Triadimefon, a sterol-inhibiting systemic fungicide, prevented heavy lesion formation even two days after infection (*Table 6*), indicating its curative property.

Both the methods described in the present paper should help to facilitate the screening of fungicides in the laboratory. The leaf disc method gave the closest approximation to the performance of the fungicides in the field⁶. The cellulose film method saves considerable trouble and cost in growth medium preparation; it is easy to perform as well as to examine under the microscope. It has other advantages in that it can also provide information on the fungicidal and fungistatic effects of the fungicides and their persistence. The fact that the film can be stained and the spores fixed for subsequent examination is another advantage. Using these methods the present study reveals

for the first time some of the properties of fungicides currently recommended for SALB control.

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Thermoplastic Elastomers I. Effect of Processing Variables on Tensile Properties of Natural Rubber/Polypropylene Blends

S. AL-MALAIKA* AND E.J. AMIR*

The effect of processing conditions and type of mixers on the mechanical performance of different compositions of natural rubber/polypropylene (NR/PP) blends are investigated. The use of 0.3% dicumyl peroxide in 60% natural rubber blends under optimised processing conditions resulted in the best mechanical performance of the blend. High shearing rate mixers (Buss-Ko kneader) afforded blends with higher initial mechanical performance compared with a laboratory-scale internal mixer (Hamptden-RAPRA torque rheometer). The evidence presented indicates the lack of interpolymer formation during the mechano-chemical process although a small amount of NR undergoes crosslinking during the processing operation. Both melt stability and mechanical properties of NR/PP blends are adversely affected on remoulding: reinjection showed much greater deterioration compared to recompression, albeit high initial mechanical properties of the injection moulded samples.

A basic requirement of a thermoplastic elastomer is the formation of crosslinks which are stable at room temperature but become unstable at processing temperatures. Thus thermoplastic elastomers exhibit both the characteristics of vulcanised rubber at room temperature and thermoplastics processibility at elevated temperatures. In the case of polypropylene-based thermoplastic elastomers, the micro-crystalline domains in polypropylene (PP) offer 'pseudo-crosslinks' which in turn are responsible for the stiffness and strength of the blends¹. These blends (e.g. NR/PP) have two distinct advantages over other thermoplastic rubbers; they are made from relatively low cost materials and they have low densities.

The characteristics of polyolefin thermoplastic elastomers depend greatly on the processing method used for their fabrication. Like other polyblends², the polyolefin thermoplastic elastomers may be produced by mechanical blending³, whereby the two different polymers are subjected to high shearing forces in a thermoplastic processing machine at a temperature above their glass transition.

Under such processing conditions, chain scission of both polymers takes place and leads to the formation of two different active macro radicals. In the absence of oxygen, recombination of these radicals yields block- or graft-copolymers⁴.

To achieve enhanced mechanical performance of polymer blends, the two phases must be compatible to a certain extent. An external solid phase dispersant is used to increase the compatibility between the two phases⁵. Blends based on NR/PP thermoplastic elastomers, on the other hand, show good mechanical performance even in the absence of an external solid phase dispersant³. The question arises as to whether an interpolymer formation due to reactions between the two polymeric phases during processing serves as an 'internal' solid phase dispersant.

The purpose of the present work is two-fold. First, to examine the question of interpolymer formation under a wide range of processing conditions and to study the effect of these conditions on the mechanical and long-term

*Department of Molecular Sciences, Aston University, Aston Triangle, Birmingham, B4 7ET, United Kingdom

ageing performance of the blends before and after various remoulding cycles (the present investigation) and secondly, to evaluate the use of NR/PP thermoplastic elastomers as solid phase dispersant for other thermoplastic-based polyblends (Part II).

EXPERIMENTAL

Materials

The following polymers were used: stabilised PP (HW 25) supplied by ICI Ltd, natural rubber (SMR 5) supplied by MRPRA and ethylene-propylene-diene monomer supplied by Exxon Chemicals Ltd under the trade name Vistalon 6505. Benzoyl peroxide (ex. BDH) and dicumyl peroxide (ex. Hercules) were used as received without further purification.

Polymer Processing

Processing was carried out either in a closed mixer of a Hampden-RAPRA torque rheometer or in a Banbury mixer or extruded in a Buss-Ko kneader, at different temperatures (160°C–180°C) and times (5–11 min). The polymer was then either compression moulded at 180°C into sheets of thickness 200 μm as described previously⁶ or injection moulded on an Edgwick 1214 HY injection moulding machine using barrel temperatures of 170°C, 180°C, and 200°C, mould temperature of 60°C, injection pressure of 47 MPa, screw speed of 50 r.p.m. and cooling time of 16 s. To prepare NR/PP blends in the presence of peroxides, the two polymers were first blended (without the peroxide) for 3 min at the required processing temperature. At the end of this period the required amount of peroxide was added and the processing was continued for various periods of time up to 11 min.

Tensile properties. Tensile tests were carried out on an Instron tensile tester (Model TMTS) using cross head speed of 3 cm per minute at 20°C. Six samples were tested for each measurement.

Melt rheology. Both the melt flow index (MFI) and viscosity of the polymer melt under

a range of shear rates at a given temperature were investigated. Measurement of the melt viscosity was carried out on a Weissenberg rheogoniometer which is basically a cone and plate viscometer. The flat platen remains stationary while the conical platen moves with an angular velocity (β) which can be regulated. The temperature was set at 230°C (similar to that used for MFI determination) and a rotational force was applied. The sample (processed in a torque rheometer and compression moulded into film, 20 μm thick) was placed between the two platens and was allowed to reach the test temperature (230°C). Viscosity measurements were carried out at different shear rates (*Equation 1*). Viscosity of the melt was calculated⁷ according to *Equation 2*:

$$\text{Shear rate } (\gamma) = \frac{360}{\alpha t} \text{ s}^{-1} \quad \dots 1$$

$$\text{Viscosity } (\eta) = \frac{t \times \alpha \times \Delta T \times K_t}{94.25 \times d^3} \text{ poise} \quad \dots 2$$

where the value of

t is dependent on the angular rotation and its value (in seconds per revolution) is calculated from the gear setting of the rheogoniometer

α is angle of cone which is $4^\circ 8'$

ΔT is the movement of the torsion head transducer (in thousandths of an inch),

K_t is torsion head constant (dyne cm per thousandths of an inch of movement of torsion head transducer) and is 3.372×10^4

d is diameter of platens which is 2.5 cm.

MFI measurements were done on a Davenport melt flow indexer at 230°C using a load of 50 Newton. Calculated MFI values are the average of five measurements for each sample.

Molecular Weight and Gel Determination

Molecular weight distribution of the soluble fraction (in tetrahydrofuran) of processed

polymer samples was determined by RAPRA using gel permeation chromatography. In these analyses, tetrahydrofuran was used as a solvent and polystyrene for the purpose of calibration. Solvent insoluble gel was measured by dissolving 0.5 ml of processed polymer in 50 ml tetrahydrofuran (90°C, 60 min) followed by filtration under nitrogen. The gel formed was vacuum-dried to a constant weight.

Determination of Insoluble Bound Natural Rubber

The extent of insoluble bound NR on PP was determined as follows: decaline (50 ml) was added to 0.5 g of NR/PP (60/40) blend and the solution was heated to 170°C under nitrogen until all the polymer had dissolved. On cooling, a mixture of PP and any insoluble 'bound' NR precipitated out while the soluble unbound NR remained dissolved in decaline. The precipitate was filtered and redissolved. This was repeated three times and the final precipitate was dried to a constant weight. The bound NR was calculated as shown below,

$$\text{Percentage bound NR} = \frac{A - B}{A} \times 100 - 40\%$$

where A is the weight before extraction

B is the weight after extraction

40% is PP fraction in the blend.

RESULTS AND DISCUSSION

Effect of Processing Variables on Natural Rubber/Polypropylene Blends

The effect of processing conditions (temperature and time using torque rheometer) on the mechanical performance of various compositions of NR and PP (compression moulded samples) was studied. *Figure 1* shows the effect of varying the composition of NR/PP and the effect of processing temperature on the tensile strength of the blends. It is clear that increasing PP content in the composition increases the tensile strength of the blends under the different temperature conditions used; the tensile

strength of PP alone is much higher than that of NR. Moreover, all blends processed at 160°C offered slightly higher tensile strength than those produced at higher temperatures. At lower temperatures, the viscosity of the blend is higher (see inset *Figure 1*) leading to higher shear rates. This may contribute to more homogeneous dispersion between the two phases with an overall improvement in mechanical performance.

The effect of processing time (at all temperatures used) on the tensile strength of the blends is less pronounced. Slightly better performance is obtained with samples processed for 7 min and this condition was subsequently used. In order to choose the optimum composition of NR/PP which produces a thermoplastic rubber, the tensile stress of different blends processed under the above conditions (160°C, 7 min) was plotted against their elongation at break (*Figure 2*). The tensile properties of blends containing low concentrations of NR (e.g. 40%) are typical of thermoplastics, *i.e.* high tensile strength and low elongation at break. This suggests that the dominant phase here is PP. On the other hand, the tensile properties of blends containing high concentrations of NR (e.g. 70%) are typical of uncrosslinked rubbers, *i.e.* low tensile strength and high elongation, suggesting that the dominant phase is NR. The observed tensile properties of blends containing 60% NR support the formation of a thermoplastic rubber. It was shown previously³ by scanning transmission electron microscopy that both phases of a 60/40 NR/PP blend, processed in an internal (Banbury) mixer, are essentially continuous.

Interpolymer Formation in Natural Rubber/Polypropylene Blends

It has been shown that addition of solid phase dispersants to polymer blends enhances their mechanical performance⁵. Mechanically formed NR/PP blends may inherently contain an interpolymer which acts as an 'internal' solid phase dispersant and may therefore contribute to improvements in mechanical properties of these blends. This possibility was examined in all the NR/PP

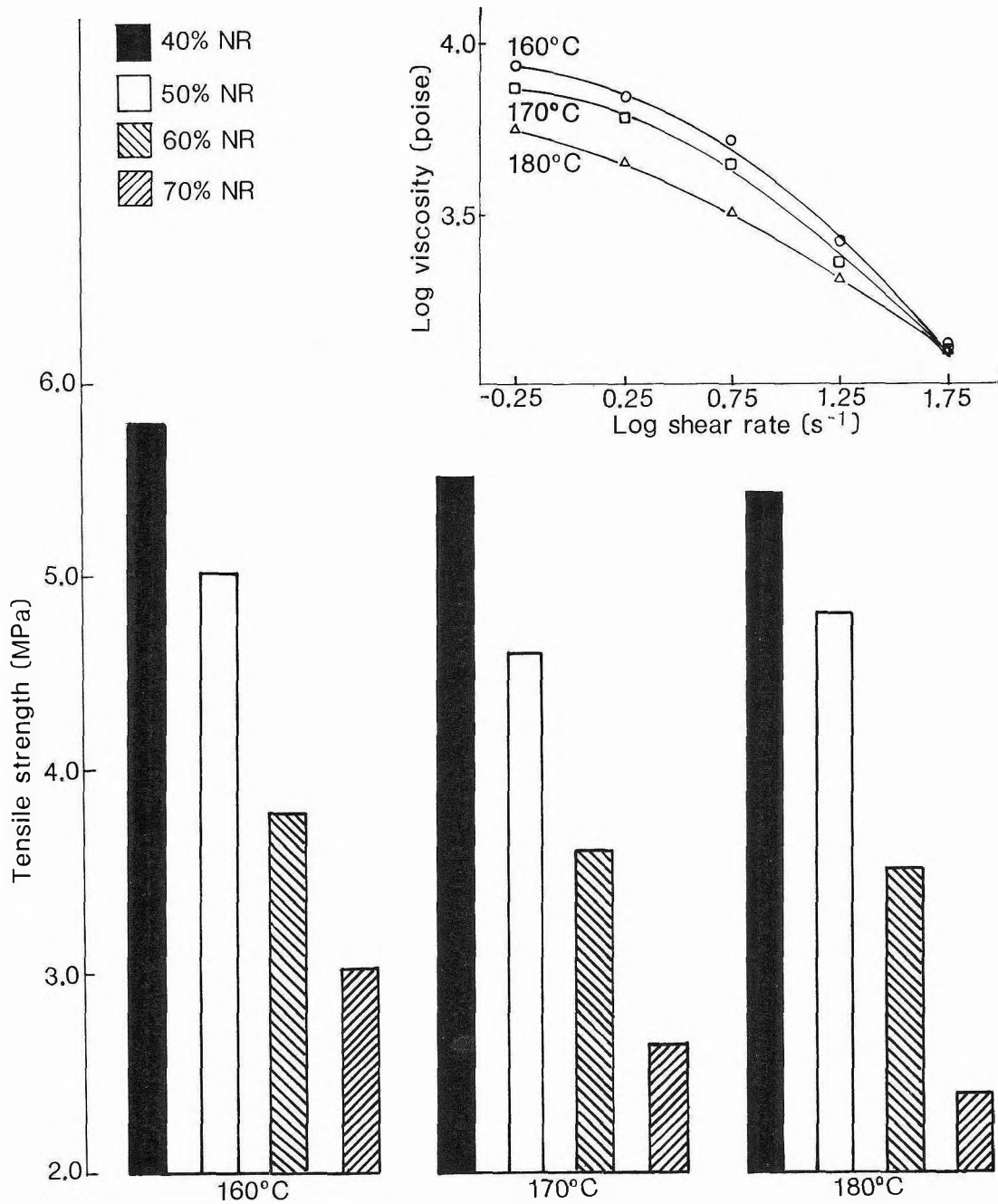


Figure 1. Effect of composition of NR/PP blends on their tensile strength when processed in torque rheometer at different temperatures for 7 min. Inset shows the effect of processing temperatures on the melt rheology of NR/PP blend containing 60% NR (processed for 7 min).

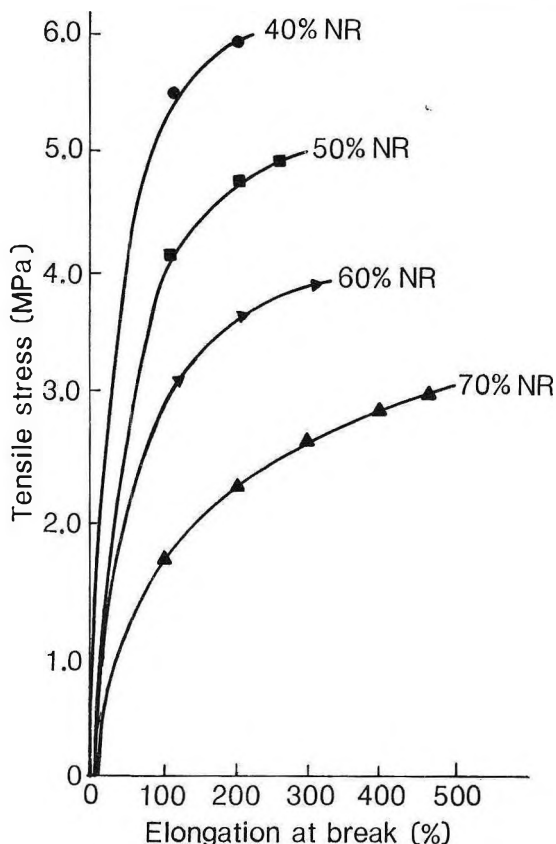


Figure 2. Stress-strain curves of different compositions of NR/PP blends processed at 160°C for 7 min.

compositions used. Figure 3 shows the effect of processing temperature and time (compression moulded samples processed in torque rheometer) on the molecular weight of extracted NR/PP compositions containing 70% and 40% NR. It is clear that processing at higher temperatures leads to a decrease in molecular weight of the soluble fractions of the blends; the effect is more pronounced with higher NR content. On the other hand, increasing PP content in the blend is accompanied by a decrease in the molecular weight under all processing conditions (see inset).

Measurement of the amount of insoluble 'bound' NR shows that, although the overall percentage of bound NR in all the compositions

and under the different processing conditions used is small, its percentage decreases with increasing PP content in the blends (Figure 4). The observed reduction in molecular weight of NR/PP blends when the PP content is increased (see inset Figure 3) is accompanied by a concomitant reduction in viscosity which leads to lower shearing forces. However, since the shearing forces exerted during the processing operation play an important role in the formation of macro-radicals, and ultimately to the interchange of the mechano-chemically formed macro-radicals of both polymer components of the blend, lower shear forces in blends containing higher PP contents must contribute to lower amounts of the interpolymer formed [as measured from the insoluble (percentage bound) NR in these blends, see Figure 4]. The very small amount of insoluble NR formed under the above processing conditions is not likely to contribute, to any significant extent, to the enhancement of mechanical properties of these blends. The relation between the insoluble NR and the mechanical performance of NR/PP (60/40) blends, when the processing operation is optimised, and hence its role on the performance of the blend is discussed in the next section.

Effect of Free Radical Initiators on Performance of 60/40 Natural Rubber/Polypropylene Blend and Role of Interpolymer Formed

The effect of free radical initiators on mechanical performance of NR/PP blends containing 60% NR was investigated. Benzoyl peroxide and dicumyl peroxide were examined. Figures 5 and 6 show the effect of the above peroxides on tensile strength of the blends. It is clear that benzoyl peroxide does not offer a significant increase in tensile strength (Table 1). There is, however, a small but steady increase in the amount of insoluble ('bound') NR with increasing concentration of this peroxide (Figure 5). Figure 6 shows that dicumyl peroxide has a more significant effect on the tensile behaviour (Table 1) of the NR/PP blend, at all processing temperatures, with marked improvements obtained at a concentration of 0.3 p.h.r. and a processing temperature of 170°C.

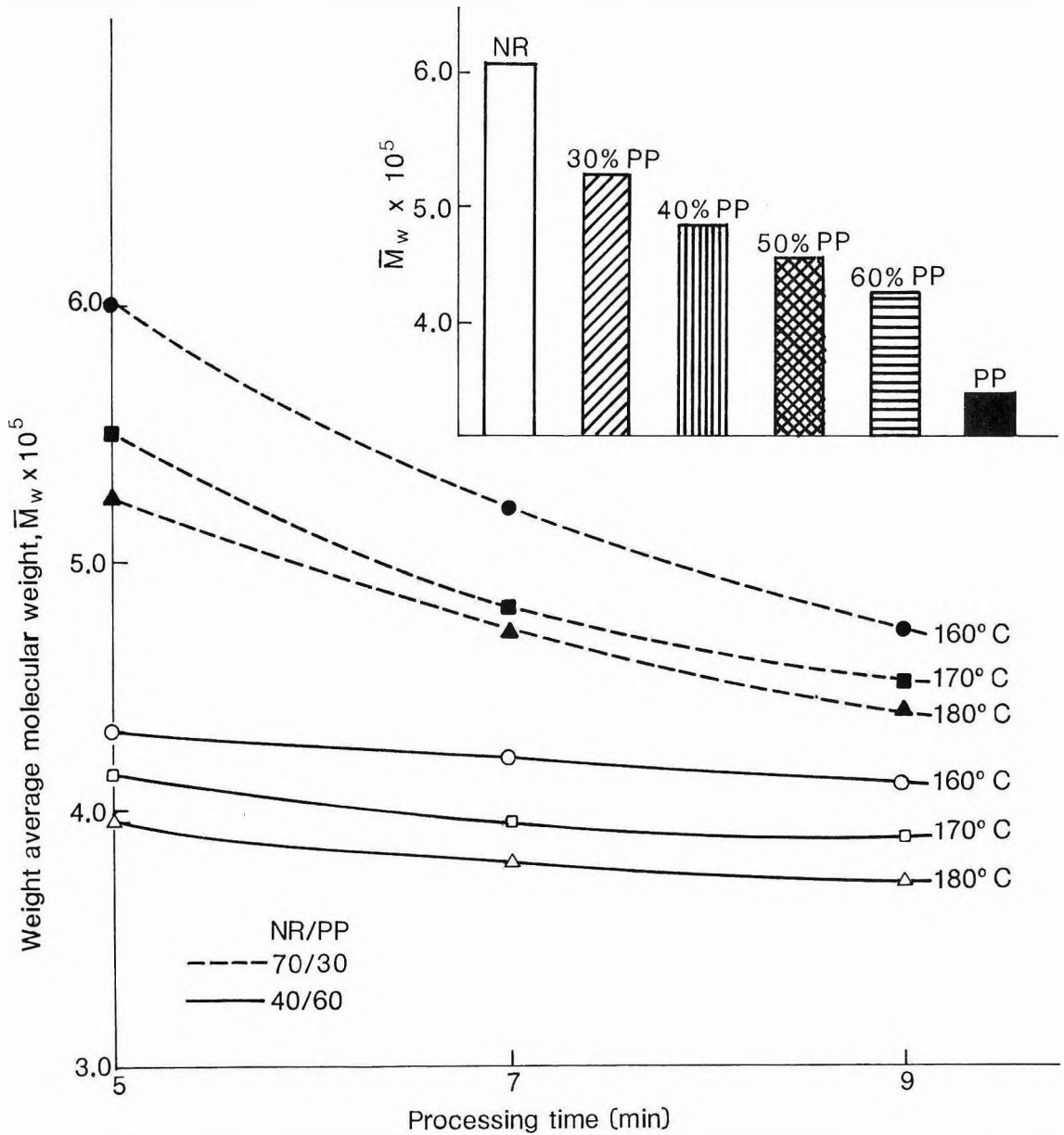


Figure 3. Effect of processing time and temperature on weight average molecular weight (\bar{M}_w) of tetrahydrofuran-soluble fraction of two different NR/PP blend compositions. Inset compares \bar{M}_w of different NR/PP compositions with those of the NR and PP controls; the blends were processed at 160°C for 7 min.

Similarly, the amount of 'bound' NR present in samples prepared with dicumyl peroxide is higher than those processed with benzoyl peroxide (Figure 7). Further improvement in

the tensile properties of the NR/PP blend, which contains the optimum dicumyl peroxide concentration (0.3 p.h.r.), was achieved by increasing processing time (Figure 8). For

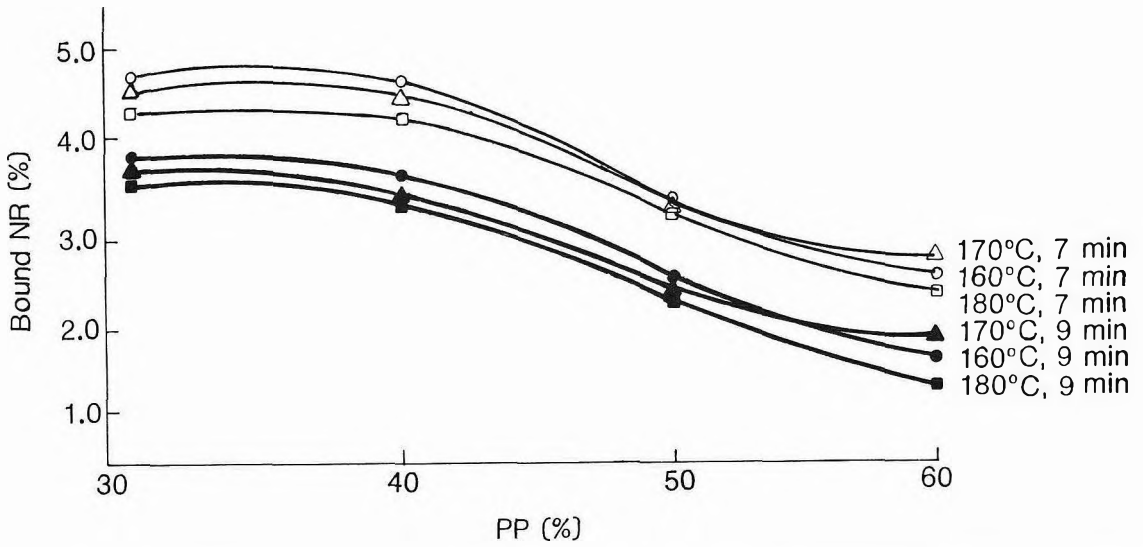


Figure 4. Effect of composition of NR/PP blends on extent of 'bound' NR formed during processing at different temperatures and times.

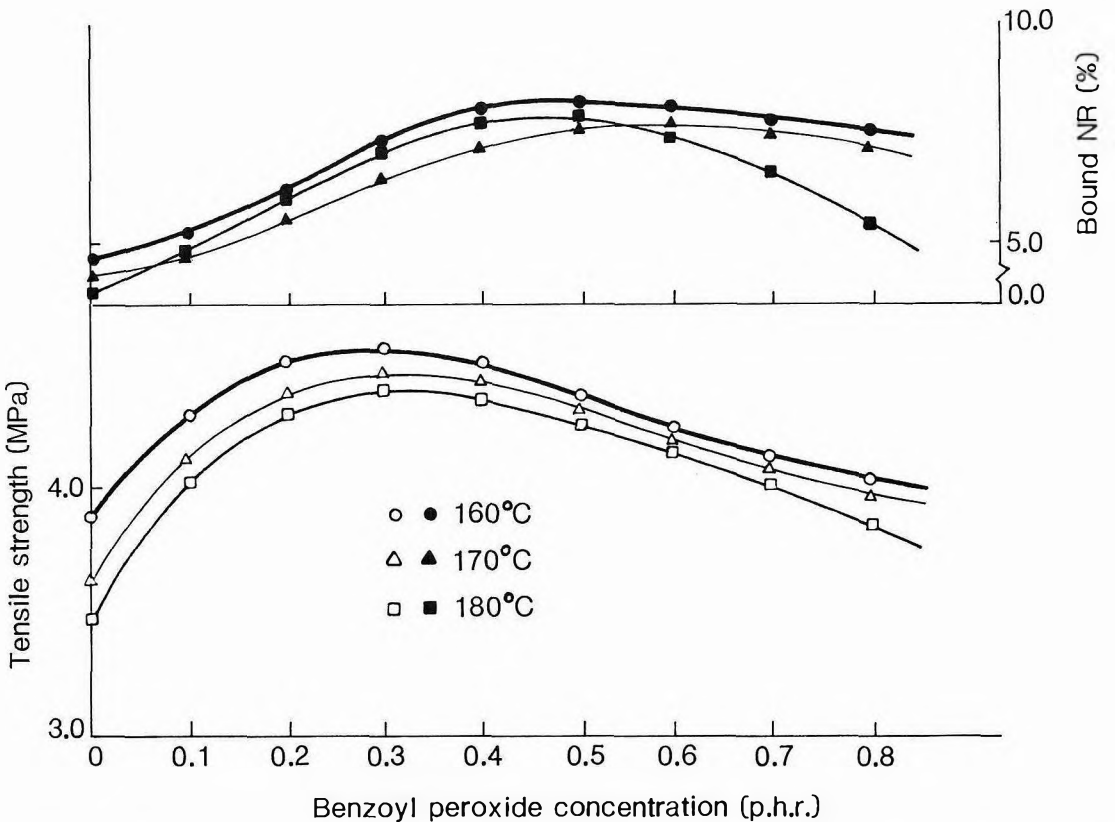


Figure 5. Effect of benzoyl peroxide concentration on extent of 'bound' NR and on the tensile strength of NR/PP (60/40) blends processed at different temperatures for 7 min.

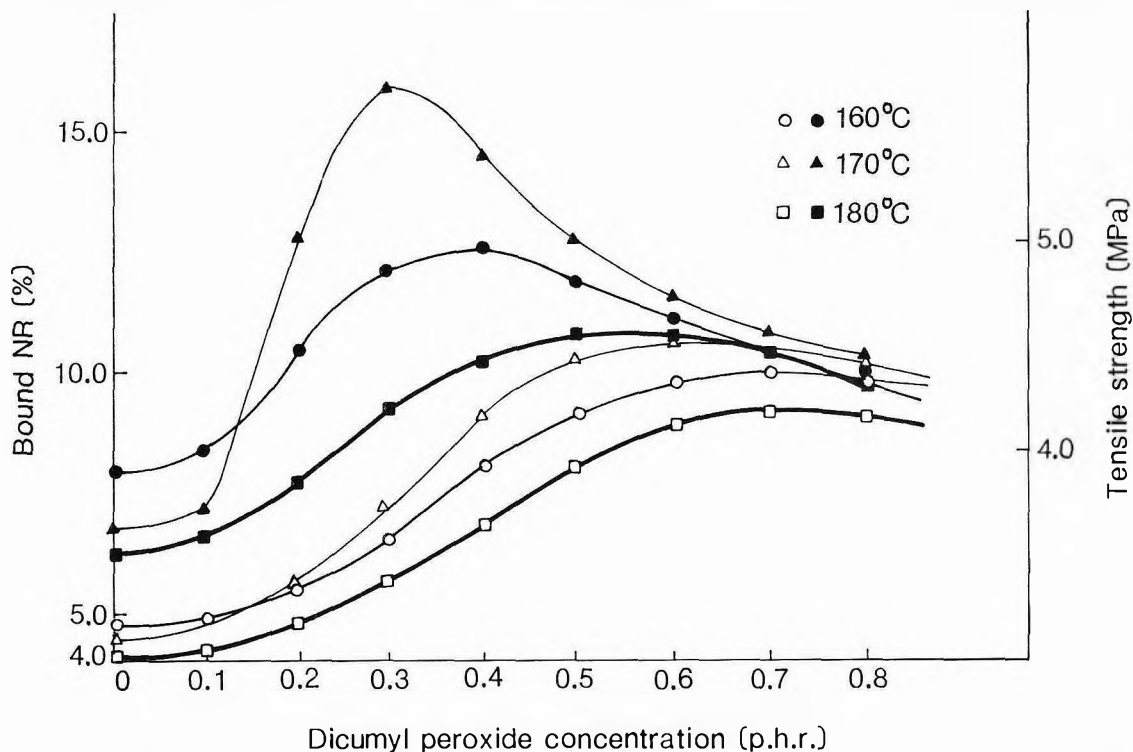


Figure 6. Effect of dicumyl peroxide concentration on extent of 'bound' NR and tensile strength of NR/PP (60/40) blends processed at different temperatures for 7 min.

TABLE 1. EFFECT OF PEROXIDES ON TENSILE STRENGTH OF NR/PP (60/40) BLENDS PROCESSED AT DIFFERENT TEMPERATURES FOR 7 MIN

Temperature (°C)	Peroxide (p.h.r.)	Improvement in tensile strength (%)
170	0.3 (dicumyl peroxide)	45
160	0.4 (dicumyl peroxide)	27
180	0.5 (dicumyl peroxide)	22
160	0.3 (benzoyl peroxide)	16

example, under the optimum processing conditions (160°C, 10 min) addition of 0.3 p.h.r. dicumyl peroxide gives rise to 88% improvement in tensile strength when compared to a similarly processed control in the absence of peroxide (or 34% improvement when compared to the 7 min processed analogue). The improvement in tensile properties under all processing

conditions, however, does not appear to be related to the insoluble 'bound' NR content formed during processing. Inset of Figure 7 for example shows this clearly at 170°C whereby the sharp drop in tensile strength, observed after the addition of 0.3 p.h.r. dicumyl peroxide, corresponds to a gradual increase in the amount of 'bound' NR. This suggests that

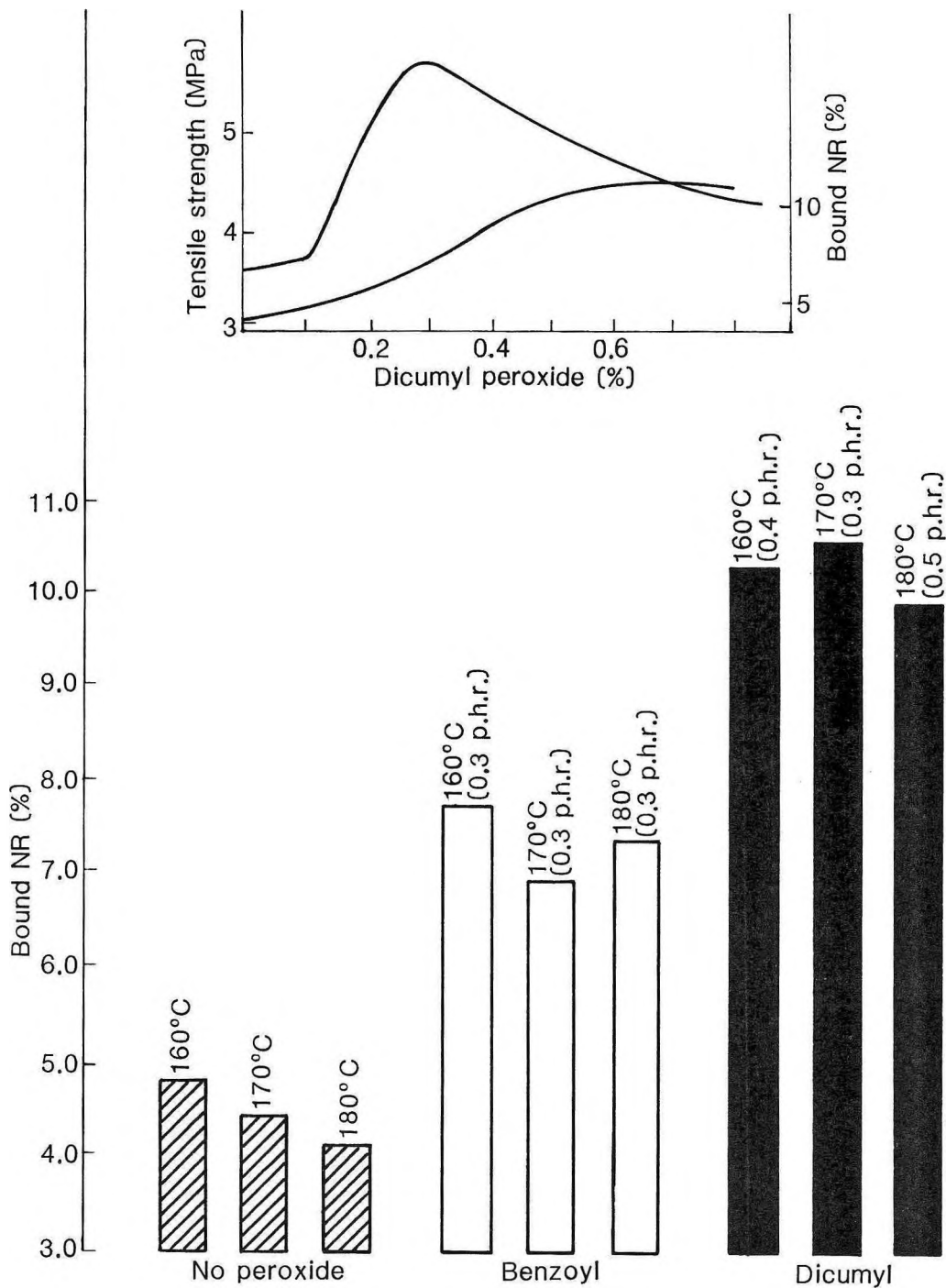


Figure 7. Maximum concentration of insoluble ('bound') NR in blends of NR/PP containing 60% NR in the presence and absence of peroxides. Blends were processed at different temperatures for 7 min. Inset shows the effect of dicumyl peroxide on extent of 'bound' NR and tensile strength of the above blend when processed at 170°C for 7 min.

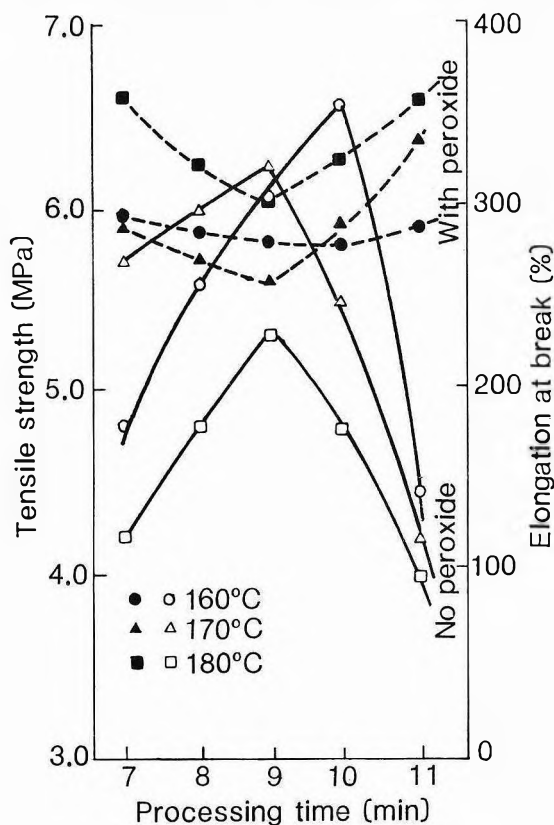


Figure 8. Effect of processing time and temperature on tensile properties of NR/PP (60/40) blends containing 0.3 p.h.r. dicumyl peroxide. Tensile strength of above samples when processed without peroxides is also shown for comparison.

the 'bound' NR as determined here is not in the form of interpolymer, but may have resulted from a chemical reaction (crosslinking) in the rubber phase itself without any significant participation from the PP phase. Peroxides are known to promote crosslinking of rubbers⁸. In the case of polyolefins, on the other hand, the effect of peroxides during high temperature processing is an increase in the level of thermal degradation⁹. If peroxides affect the components of NR/PP blends in this way then this may account for the decrease in tensile strength which is observed at higher peroxide concentrations (≥ 0.3 p.h.r.).

To examine the above possibilities, the behaviour of each component of the blend *i.e.* NR and PP, was compared with that of the blend itself under identical processing conditions and similar concentrations of dicumyl peroxide. If degradation of the counter polymer, *i.e.* PP, does take place with increasing peroxide concentration then this must be due to two factors; an increase in viscosity of the blend and the effect of peroxide on the PP phase. Figure 9 shows changes in viscosity of NR/PP blends (with 60% NR) containing different concentra-

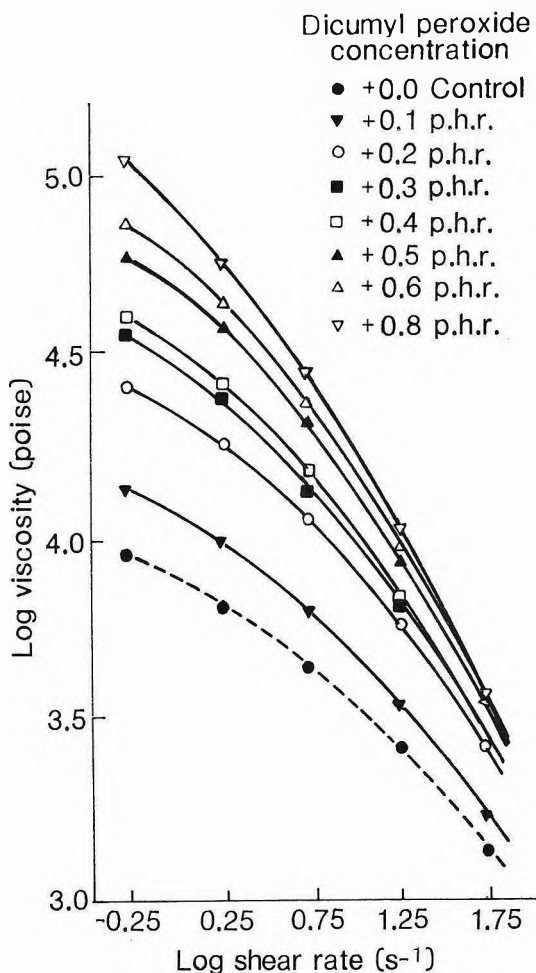


Figure 9. Effect of dicumyl peroxide on the melt rheology of NR/PP (60/40) blends processed at 160°C for 7 min.

tions of dicumyl peroxide at different shear rates. It is clear that increasing the concentration of dicumyl peroxide causes a remarkable increase in viscosity of the blends at low shear rate but this difference decreases dramatically with increasing shear rates. This is even more pronounced for blends which have higher viscosities. Increasing viscosity of the blends causes higher shearing forces which may lead to greater degradation of the PP phase. *Figure 10* compares changes in MFI of PP and NR samples processed separately in the presence of varying concentrations of dicumyl peroxide. It is clear that the MFI of NR decreases dramatically with increasing concentration of dicumyl peroxide under all processing temperatures suggesting a crosslinking reaction. In contrast, MFI of PP processed under the same conditions increased very rapidly with increasing concentration of the peroxide indicating a chain scission process. Inset of *Figure 10* shows clearly that the gel content in NR increases dramatically with increasing concentration of dicumyl peroxide while the molecular weight of the gel-free remaining solution (the soluble fraction) decreases. Increasing concentration of dicumyl peroxide, therefore, leads to the formation of an insoluble high molecular weight fraction in NR (see also *Figure 6*, note the continuous increase in the unextractable NR content with increasing dicumyl peroxide concentration in the blend). This must give rise to the overall observed decrease in MFI of these NR samples. In the case of PP, on the other hand, no gel was formed under all concentrations of dicumyl peroxide used and the weight average molecular weight of PP (all of which is soluble) decreases with increasing concentration of dicumyl peroxide. This finding is in accord with the earlier observation where MFI of these samples show an increase with increasing peroxide concentration (*Figure 10*). These observations are attributed to the degradation of PP by a chain scission process. High temperature thermal processing of polyolefins may lead to oxidative degradation (*Scheme 1a*), crosslinking (*Scheme 1b*) or chain scission (*Scheme 1c*)^{10,11}. Crosslinking reactions take place only under restricted oxygen access and the structure

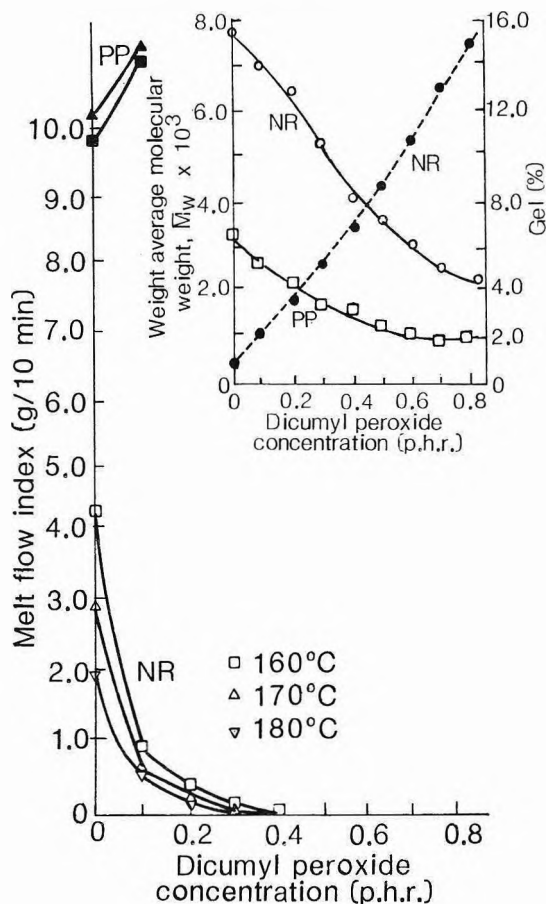
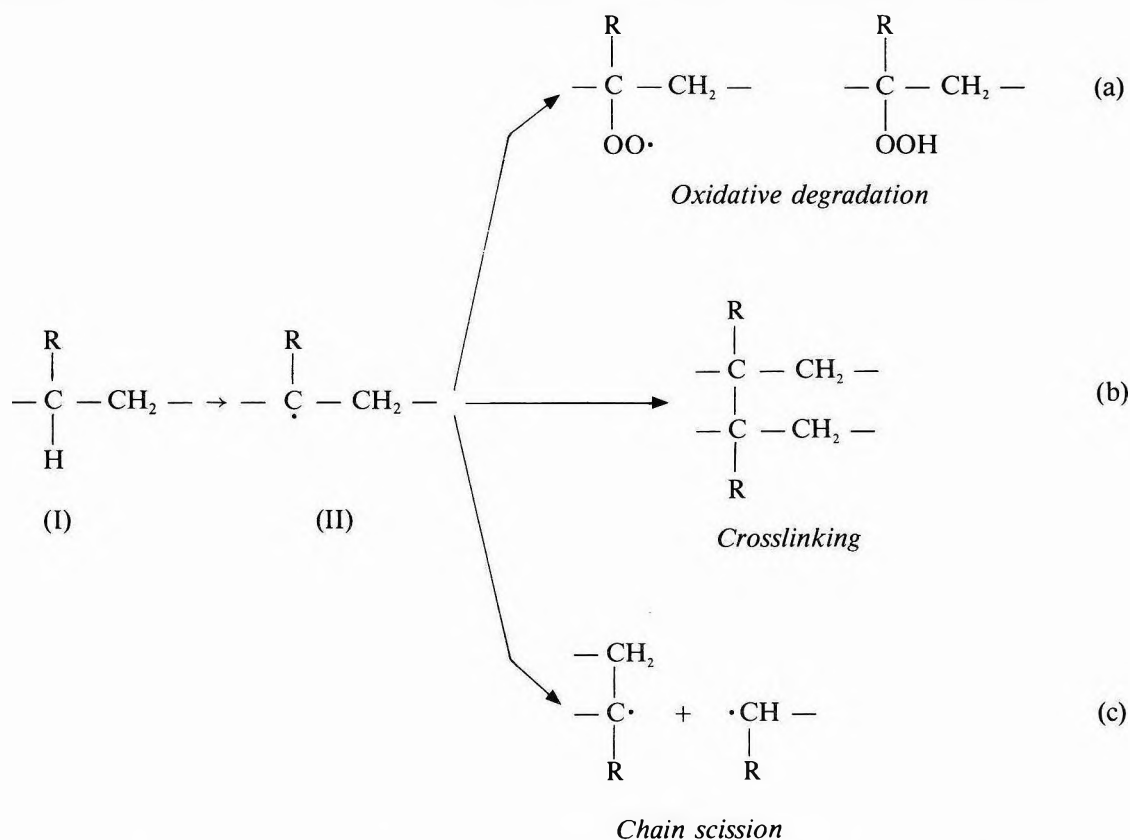


Figure 10. Effect of dicumyl peroxide on melt flow index of NR and that of PP processed separately at different temperatures. Inset shows the effect of dicumyl peroxide on weight average molecular weight of tetrahydrofuran-soluble fraction of PP and of NR processed separately at 160°C for 7 min. Amount of gel formed in NR is also shown.

of the R group (*Scheme 1, I*) determines the preferred reaction pathway. In the case of PP ($R = CH_3$) the positive induction effect of the methyl group facilitates a homolytic scission of the C-H bond and the tertiary macro-radical (*II*) formed will readily undergo chain scission (*Scheme 1c*) even under low partial pressure of oxygen; in the presence of oxygen, *Reaction 1a* predominates.



Scheme 1. Primary degradative processes occurring as a result of thermal processing of polyolefins.

In the light of the above results, the effect of dicumyl peroxide on the behaviour of NR/PP blends was examined. *Figure 11* shows that in NR/PP blends increasing concentration of dicumyl peroxide leads to a dramatic overall decrease in the MFI. The effect of the peroxide on MFI of the blends must then be two-fold: a reduction in MFI due to the crosslinking process in the rubber phase, and an increase in MFI (or decrease in molecular weight of the soluble fraction of the blend, *Figure 11*) due to degradation of PP contents. However, since the amount of NR in this blend is higher than that of PP, the process of crosslinking predominates as shown in *Figure 11*. The effect of degradation of PP is likely to be more important in determining the tensile properties of the blend since in such a thermoplastic

elastomer, the strength relies on the PP phase and hence a consequent drop in tensile strength of the blend after addition of 0.3 p.h.r. dicumyl peroxide is observed (*Figure 6*) even though the amount of crosslinked rubber continues to increase.

Effect of Processing and Remoulding Operations on Natural Rubber/Polypropylene

Mechanical properties and melt stability of injection moulded NR/PP samples when processed in the three different mixers at different temperatures are compared in *Table 2*. It is clear that blends processed in the Buss-Ko kneader and Banbury mixer have better initial mechanical properties than those processed in the torque rheometer. The first two processing

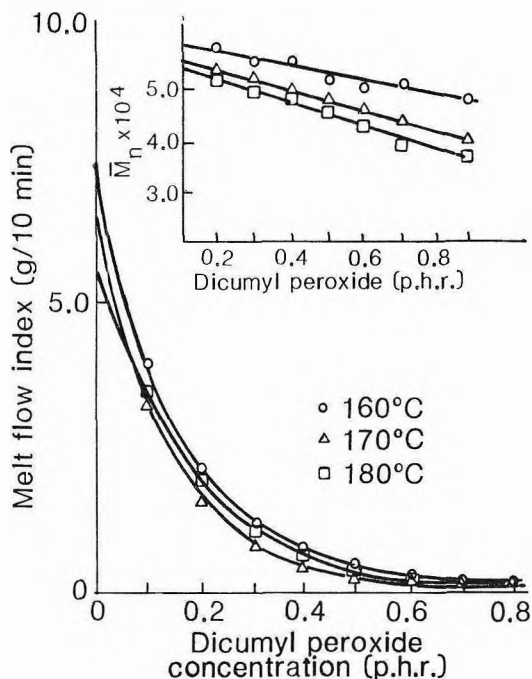


Figure 11. Effect of dicumyl peroxide on melt flow index of NR/PP (60/40) blends processed at different temperatures for 7 min. Inset shows changes in number average molecular weight of the soluble fraction of the blends under the same conditions.

machines offer higher shearing forces than the laboratory-scale internal mixer; the Buss-Ko kneader offers the highest shearing forces due to the double (reciprocating and rotating) action of the screw. The higher shearing forces exerted by the former processing machines must help in rupturing the molecular chains of NR to a larger extent than is the case in the torque rheometer leading to a decrease in viscosity of the rubber phase hence offering better dispersion of the two phases which in turn contribute to the observed higher mechanical properties in the blend. It is clear that a combination of high temperature and shearing forces reduces the thermal stability of the blends as reflected in the higher MFI values (Table 2).

Recycling of polymer blends based on combinations of polypropylene with other ther-

moplastic polymers such as polyethylene or polystyrene has been studied and antioxidants have been used to protect the blends under conditions encountered during recycling operations with the production of products with good initial and long-term performance¹². The idea of being able to remould rejects and scraps of NR/PP blends is an attractive one and is examined here. Both recompression and reinjection mouldings were investigated. Figure 12 shows the effect of ten successive recompression moulding cycles (at 180°C) on the tensile properties and melt stability of the NR/PP blends processed in the three mixers (at 160°C). It is clear that in all cases the mechanical properties are retained up to three or four recompression cycles before a sharp decline in the properties takes place. This coincides with only little changes in the MFI during the first three cycles (inset Figure 12). In this respect the behaviour of thermoplastic rubber tested here is similar to that of a typical thermoplastic in being able to be remoulded. Although during the first few recompression cycles, blends processed in the Buss-Ko kneader (where the shearing forces are high) show higher mechanical performance than when processed in a laboratory-scale torque rheometer (see, for example, tensile strength curves in Figure 12), at a larger number of recompression cycles (more than five) the curves cross over, such that performance of blends processed under conditions of high shear (Buss-Ko kneader) becomes lowest. This emphasises the importance of the initial thermal history on subsequent operations. Initially, the more homogeneous mixing offered by processing mixers with high shearing forces is the main contributory factor to the better initial properties. However, at the same time, under these high shear rate conditions the thermal stability of the blends is lower than if processed under lower shearing conditions as reflected by the higher MFI (inset Figure 12). This thermoxidative instability becomes the dominating factor responsible for the much lower strength of the blends observed after larger numbers of recompression moulding cycles.

Figure 13 shows the effect of reinjection moulding on the behaviour of NR/PP blends.

TABLE 2. INITIAL MECHANICAL PROPERTIES OF INJECTION MOULDED NR/PP (60/40) BLENDS PROCESSED IN BUSS-KO KNEADER, BANBURY MIXER AND A RAPRA-HAMPDEN TORQUE RHEOMETER AT DIFFERENT TEMPERATURES

Mechanical properties	Processing temperatures (°C)		
	150	160	170
Torque rheometer			
Tensile strength (MPa)	—	7.60	7.30
Elongation at break (%)	—	390	350
Tensile modulus (MPa)	—	63	60
Flexural modulus (MPa)	—	145	136
Flexural strength (MPa)	—	13	13
MFI (g/10 min)	—	1.1	1.2
Buss-Ko kneader			
Tensile strength (MPa)	10.20	9.50	8.2
Elongation at break (%)	340	360	370
Tensile modulus (MPa)	75	70	67
Flexural modulus (MPa)	162	155	148
Flexural strength (MPa)	18	16	15
MFI (g/10 min)	1.6	1.8	2.0
Banbury mixer			
Tensile strength (MPa)	9.10	8.30	7.50
Elongation at break (%)	360	360	380
Tensile modulus (MPa)	68	65	65
Flexural modulus (MPa)	150	145	140
Flexural strength (MPa)	15	13	13
MFI (g/10 min)	1.4	1.6	1.8

It is clear that the effect of reinjection moulding on properties of the blends is much more severe than recompression moulding (shear rate exerted during injection moulding is about one hundred times higher than in the case of compression moulding). Although the initial properties of injection moulded samples are higher than the compression moulded ones (see for example inset *Figure 13*), in the case of the former there is sharp drop in properties (e.g. tensile strength) after the first three reinjection cycles, while changes in the recompression moulded samples are minimal even after seven cycles. Moreover, the high shearing forces involved in the injection moulding process contribute to a lower melt stability (higher MFI

values). Further, the extent of changes in mechanical properties with the increasing number of recycling operations of blends processed under both high (e.g. in Buss-Ko kneader) and low shear (e.g. in torque rheometer) forces is more pronounced in injection moulded samples compared to compression moulded analogues. For example, tensile strength of blends processed in a Buss-Ko kneader decrease by a factor of six after seven reinjection moulded cycles, while those processed in a torque rheometer decrease by a factor of two only at the end of the seventh cycle. This does suggest that although NR/PP blends can be reinjection moulded like thermoplastics, incorporation of antioxidants is essen-

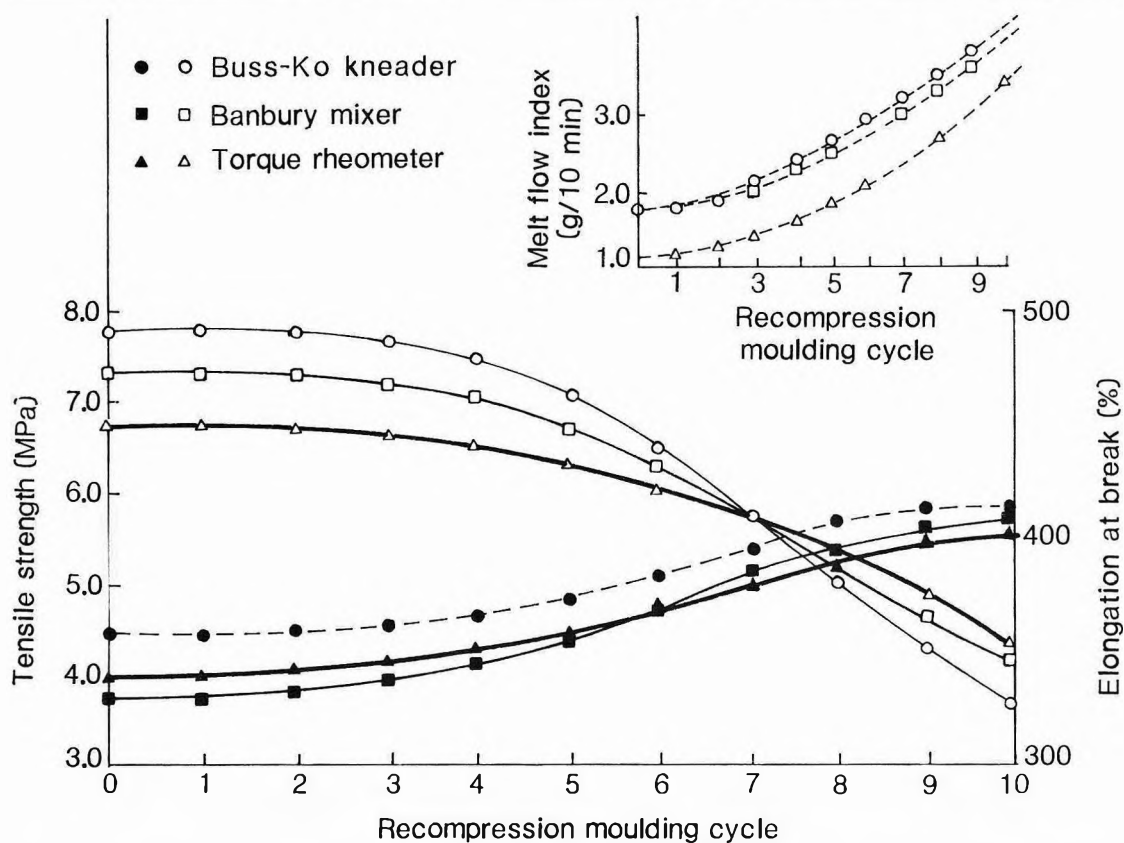


Figure 12. Effect of recompression moulding on tensile properties of films of NR/PP (60/40) blends containing 0.3 p.h.r. dicumyl peroxide processed in torque rheometer, Buss-Ko kneader and Banbury mixer. Inset shows changes in melt flow index of the same samples.

tial if the melt stability and the level of their initial mechanical properties are to be maintained throughout the reprocessing cycles.

The behaviour of the NR/PP blends under environmental conditions which may be encountered in service such as exposure to ultraviolet light and high temperatures was also examined. Figure 14 shows changes in tensile properties and the build-up of carbonyl functional groups in NR/PP compression moulded films processed in a Buss-Ko kneader and in the torque rheometer. The high photooxidative instability manifested in the rapid growth of carbonyl index may be expected due to the high levels of NR (60%) in the blend. Higher shearing forces (in Buss-Ko) which contribute

to high initial mechanical properties are also responsible for higher build-up of polymer hydroperoxides whose detrimental effect becomes very clear after the first few hours of irradiation; blends processed in a Buss-Ko kneader lose about 60% of their original tensile strength value after 11 h of irradiation while the torque rheometer-processed blends lose less than half (about 40% only) their original tensile strength under the same conditions.

Thermostability of injection moulded NR/PP samples processed in the three mixers is shown in Figure 15. In general, samples processed in Buss-Ko kneader offer higher mechanical properties than those processed in the torque rheometer. Blends in both cases

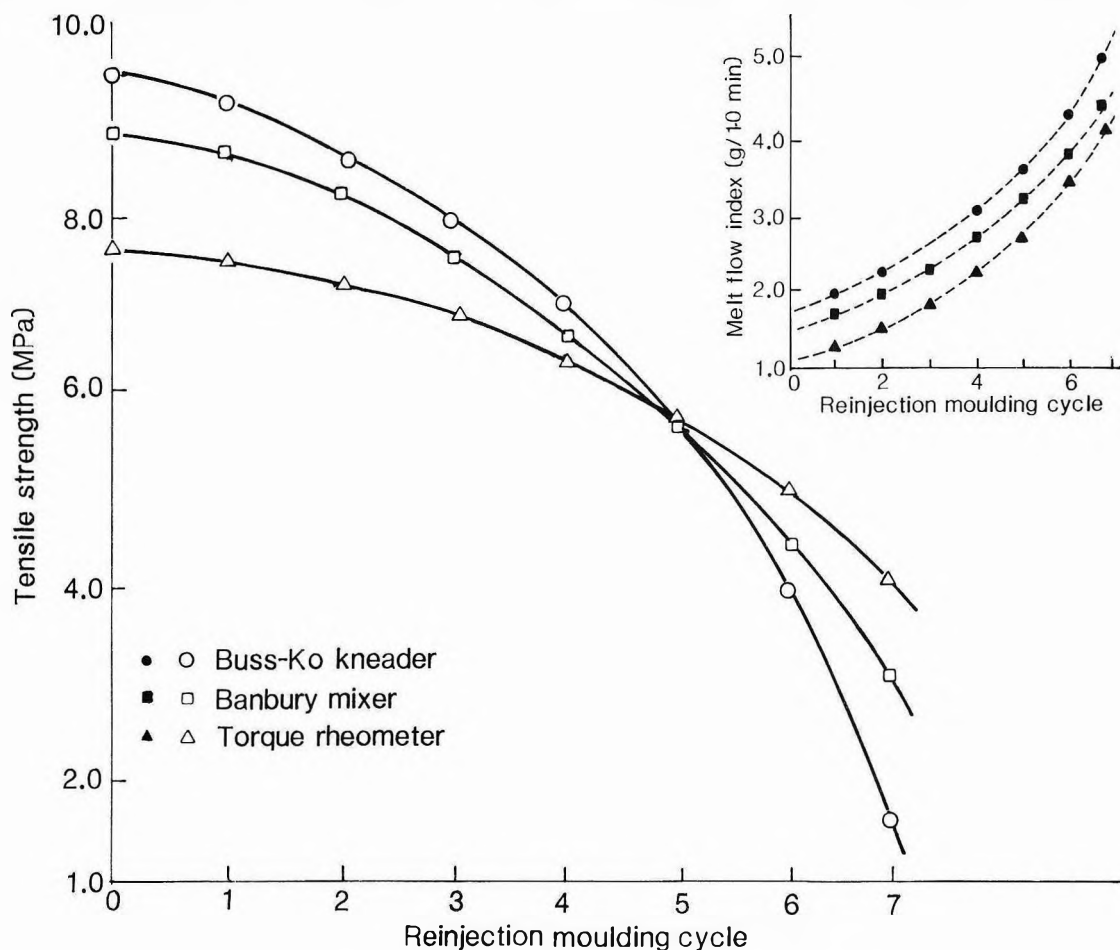


Figure 13. Effect of reinjection moulding on tensile strength and melt flow index (inset) of NR/PP (60/40) blends containing 0.3 p.h.r. dicumyl peroxide processed in torque rheometer, Buss-Ko kneader and Banbury mixer.

retain their properties for up to seven days at 70°C. However, at higher ageing temperatures considerable loss in tensile and flexural properties occur (see inset Figure 15); at 100°C for example, the tensile strength decreases by almost 50% of its initial value after three days only. The decay of properties at higher temperatures (e.g. 100°C) must be due to degradative processes in both NR and PP phases, while at lower ageing temperatures (e.g. 50°C) it is due mainly to NR. The effect of antioxidants and stabilisers on the subsequent in-service performance will be the subject of another publication.

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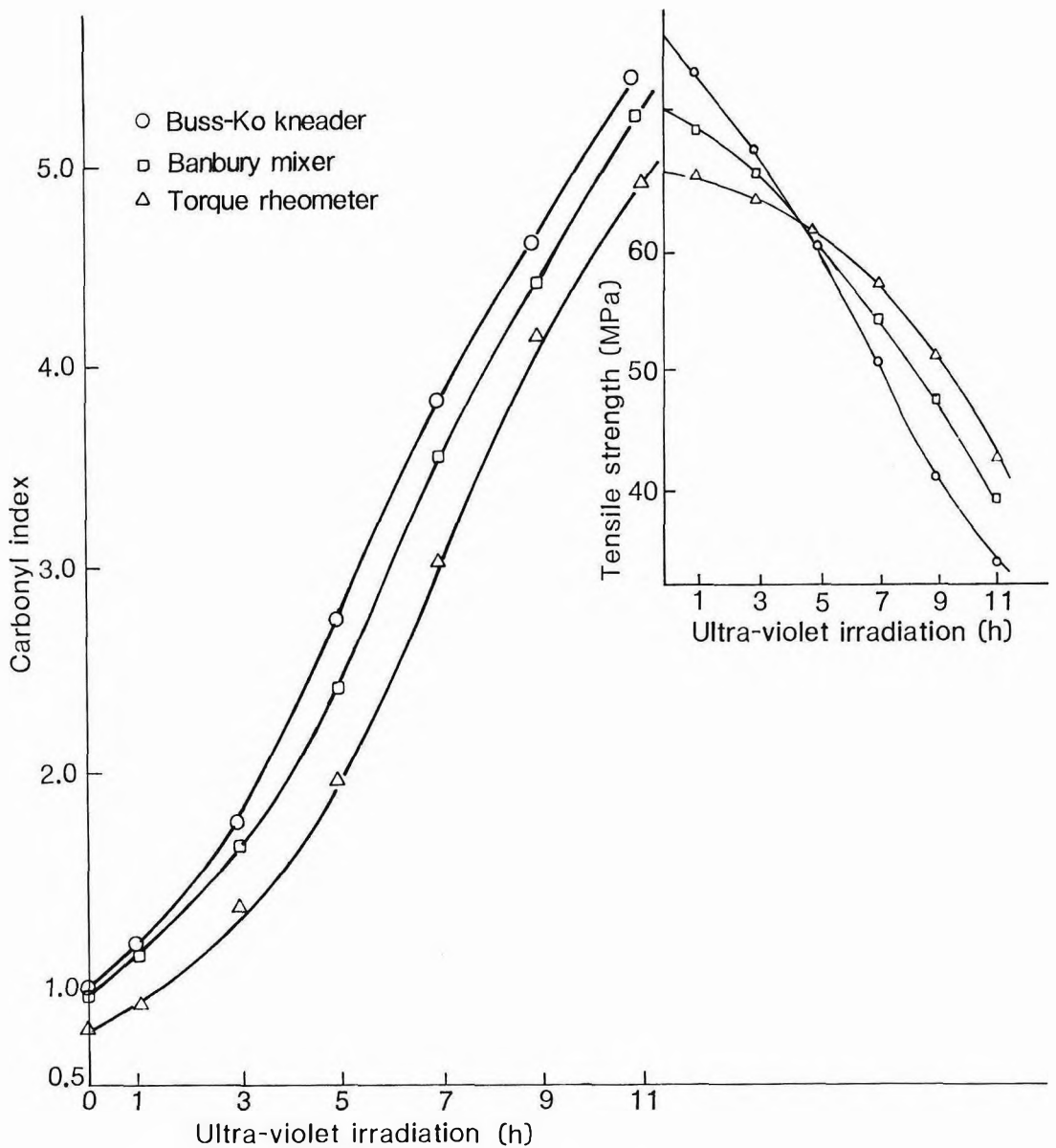


Figure 14. Effect of irradiation time on formation of carbonyl groups and changes in tensile strength (inset) of films of NR/PP (60/40) blends containing 0.3 p.h.r. dicumyl peroxide processed in torque rheometer, Buss-Ko kneader and Banbury mixer, (ultra-violet cabinet containing eight sunlamps and twenty-four actinic blue lamps arranged in symmetrical sequence was used as a source of irradiation).

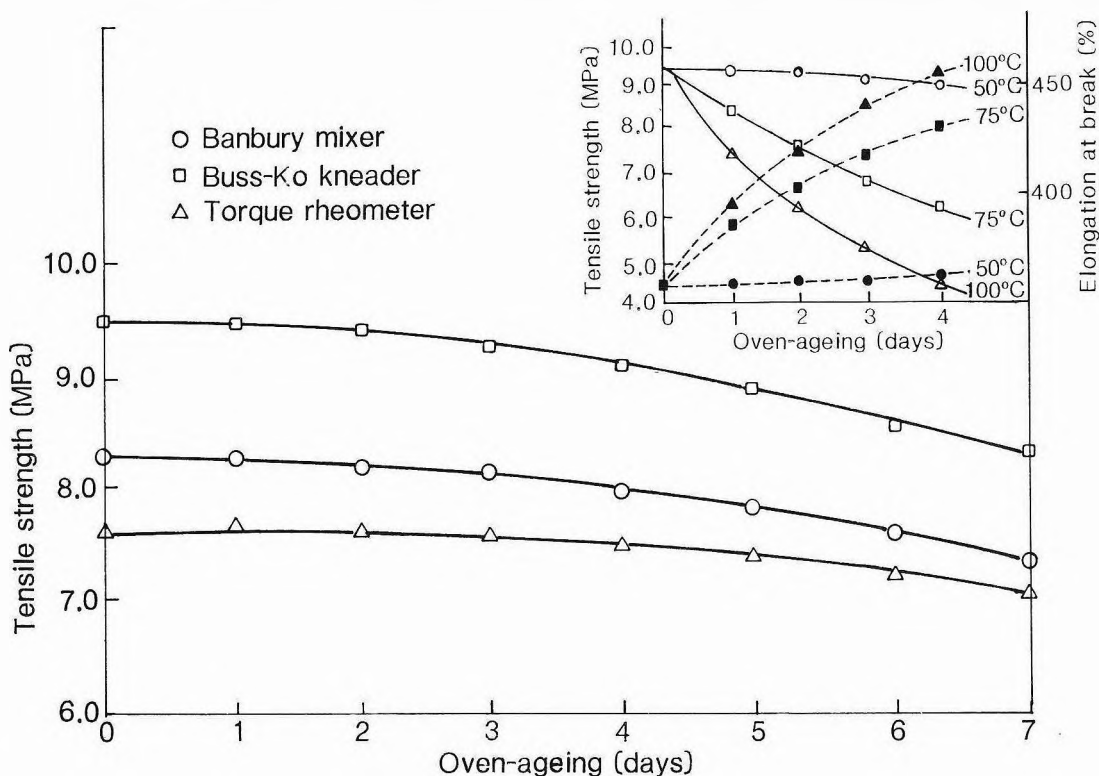


Figure 15. Effect of oven ageing (50°C , using single cell Wallace oven and air flow of 0.07 m^3 per hour on tensile strength of films of NR/PP (60/40) blends containing 0.3 p.h.r. dicumyl peroxide processed in torque rheometer, Buss-Ko kneader and Banbury mixer. Inset shows changes in mechanical properties at higher temperatures.

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Properties and Processability of High Ammonia Latices

A.D.T. GORTON* AND T.D. PENDLE*

A systematic study of the physical and chemical properties of samples of mature commercial natural rubber latex concentrate of the high ammonia variety has been carried out. More than forty parameters were measured on each of twenty latices, enabling the current range of variation in each property to be assessed. In many respects the latices were found to be relatively consistent but significantly greater variability was found in their response to the addition of zinc ammine ions. This variability is considered to relate to the variable processing behaviour sometimes observed in the user factories. The results obtained in this study did not reveal any strong relationship of zinc ion sensitivity to any other measured property. It appears, therefore, that sensitivity to zinc ions of high ammonia latex is determined by a combination of several factors the nature of which remains to be determined.

The concept of latex concentrate processability has been presented and discussed in detail in an earlier paper¹. This paper indicated the need for consistent chemical stability in latex from one batch to another, which is especially important in modern fully automated industrial processes, especially latex dipping. It is known that NR latices vary in their mechanical and chemical stability, but the latter, which is commonly equated with processability, is more variable. This is believed to be due to the unpredictability of the latex-zinc oxide, or zinc ion, interaction. It is known that dissolved zinc is capable of precipitating some of the naturally-occurring stabilisers, principally fatty acid soaps, and that this reduces stability. If the fatty acid soap content of latices was markedly variable, then this could account for irregular processability.

The previous paper in this series examined twenty-one samples of commercial low ammonia latex preserved with zinc oxide and tetramethylthiuram disulphide (LA-TZ type). Many of the common latex properties, such as mechanical stability time (MST) and KOH number in this series were found to be consistent. However, viscosity increases in the presence of zinc ammine ions (ZAAV test) were very variable, and were matched only by similar irregularity in the results for adsorbed ion

determinations. It was tentatively suggested from this data that there was a direct relationship between adsorbed soap levels and the sensitivity to zinc salts.

In this paper, the results of a systematic study of twenty samples of commercial high ammonia (HA) latex are summarised. The study included the measurement of most of the *ISO 2004* properties² and trace element levels, together with chemical stabilities, serum anion levels, and surface ion estimation by conductimetric titrations. The influence of these properties on the mechanical and chemical stabilities of the latices is discussed. The results obtained here are briefly compared with those obtained for the LA-TZ series of latices.

EXPERIMENTAL

Samples of HA latex concentrates were obtained from European dealers in the period September 1982 to July 1985 and are believed to be representative of the bulk material imported at that time. The latices all generally complied with the requirements of the *ISO 2004* specification.

Tests for total solids content (TSC) dry rubber content (d.r.c.), KOH number, volatile fatty acid number (VFA), MST, and alkalinity

*Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford, United Kingdom

were carried out according to the methods of *ISO 124*, *ISO 126*, *ISO 127*, *ISO 506*, *ISO 35* and *ISO 125* respectively. Viscosity measurements were made using a Brookfield LVT viscometer at 25°C at 6 r.p.m. and 60 r.p.m., both on undiluted samples and on samples diluted to 59.0% d.r.c. with water. Stability to zinc was assessed using the German³ ZST test and a viscosity increase (ZAAV) test. In the latter, the latex was mixed with 0.7 p.p.h.r. of zinc, added as ammoniated zinc acetate (ZAA) solution, and diluted with water to 55% TSC. The viscosity of the mix was measured after 1 h and 24 h of storage at 25°C. The ZAA solution used was prepared as follows:

Zinc acetate dihydrate (analytical reagent grade)	274.4 g
0.880 ammonia solution	400.0 g
Water	to 1000 ml

This solution is 1.25 *M*, or 8.2% by weight, with respect to zinc.

The preparation of serum samples and the analysis of serum anions were carried out as previously described⁴. Carbonate levels were determined by the method of Calvert and Smith⁵.

Total nitrogen contents were determined on total solids films prepared after addition of 1% potassium hydroxide to the latex to eliminate ammoniacal nitrogen. Potassium and magnesium contents were measured on separately prepared total solids films with no addition of potassium hydroxide. Measurements of nitrogen and potassium were also made on the cream layer obtained after diluting the latex to 10% d.r.c. with 0.3% potassium alginate solution and centrifuging at 3000 r.p.m. in a bench centrifuge. Conductimetric titrations with potassium hydroxide and ammoniated zinc acetate were carried out as described previously⁶.

RESULTS AND DISCUSSION

Latex Properties Defined in *ISO 2004*

Many of the latex characteristics specified in *ISO 2004* have been determined and the results

are listed in *Table 1*, together with the mean and coefficient of variation (CV) values.

It can be seen from the results that the factors which may be regarded as totally within the control of the producer, *i.e.* TSC, d.r.c. and alkalinity, showed a relatively low degree of variation. However, all but one of the samples had d.r.c. values under 60.0% and were thus technically outside the *ISO 2004* limit. Factors which are only partially within the control of the producer, *i.e.* MST and VFA number, revealed a greater variation but were still relatively consistent. All the latex samples had mechanical stabilities appreciably above the 650 s limit in *ISO 2004* (1979) but *Sample 13* had a VFA number approaching the specification limit and was obviously not well preserved.

Total Anion Concentrations (KOH Numbers)

A further comparison of potentiometric and conductimetric KOH titrations has been carried out and the results are given in *Table 2*. These confirm the earlier conclusion⁶ that conductimetry generally gives higher values than potentiometry in KOH titrations and showed that the increment averaged about 13%, but with a fairly wide variation. The CV values also indicate that conductimetry gives a greater variation in KOH numbers than potentiometry. As with LA-TZ latices, the CV value of conductimetric KOH numbers is closer to the CV value found with the serum ion concentrations than to that of the ISO method.

Volatile Fatty Acid Contents

The VFA numbers determined by the ISO method, *i.e.* by coagulation and acidification followed by steam distillation, may be compared with the volatile acid content determined by ion chromatography (IC). Previously¹ the ion chromatography results were consistently lower than those of the ISO method and the new data shows the same trend (*Table 3*). The VFA numbers of these HA latices were generally higher and more variable than the LA-TZ latices previously examined.

Viscosity Characteristics

The results of the viscosity measurements are shown in *Table 4*. The values found were quite

TABLE 1. SOME ISO 2004 SPECIFIED PROPERTIES OF HA LATICES

Latex sample	TSC (%)	D.r.c. (%)	Non-rubber solids (%)	Alkalinity (% aq phase)	pH	VFA (No.)	MST (s)
1	61.61	59.85	1.76	2.00	10.60	0.10	1020
2	61.31	59.92	1.44	1.93	10.60	0.10	1080
3	61.43	59.38	2.05	1.52	10.55	0.04	1070
4	61.27	59.79	1.48	1.42	10.53	0.03	1250
5	61.44	59.84	1.60	1.39	10.60	0.03	1160
6	61.08	59.62	1.46	1.93	10.70	0.06	1380
7	61.35	59.75	1.60	2.01	10.50	0.03	880
8	60.88	59.25	1.63	1.84	10.48	0.05	1185
9	61.30	59.82	1.48	1.92	10.72	0.06	1620
10	61.35	59.89	1.46	1.81	10.77	0.05	1410
11	61.34	59.97	1.37	1.85	10.80	0.09	1130
12	60.83	59.57	1.26	1.78	10.80	0.05	1065
13	61.75	60.17	1.58	1.84	10.78	0.19	710
14	61.82	59.71	2.11	1.68	10.87	0.04	1140
15	61.18	59.61	1.57	2.00	10.90	0.12	1080
16	61.59	59.92	1.67	1.67	10.87	0.04	1450
17	61.15	59.56	1.59	2.06	11.05	0.07	1485
18	61.60	59.74	1.86	1.70	10.68	0.06	863
19	60.96	58.92	2.04	1.16	10.10	0.05	1530
20	60.90	59.05	1.85	1.71	10.18	0.08	848
Mean value	61.31	59.69	1.64	1.76	10.65	0.07	1168
CV (%)	0.47	0.53	14.3	13.4	2.2	57.7	21.3
Specification limit (optional)	61.5 min.	60.0 min.	2.0 max	1.58 min.	—	0.20 max	650 min.

consistent and showed relatively little variation from sample to sample. They were also broadly similar to the results obtained with LA-TZ latices.

Stability to Zinc Ions

Each latex was tested for mechanical stability in the presence of zinc oxide (ZST) and for viscosity increase in the presence of ammoniated zinc acetate solution (ZAA), as described in the experimental section. The results of these tests are given in *Table 5*.

As for the LA-TZ latices, ZST values showed a moderate variability but the ratio of ZST to MST was less variable and comparable with the variability of the MST values (*Table 1*). The viscosity increases in the ZAAV test, however, showed moderately high variabilities which did not correlate with the variations in ZST values. It is noticeable that the viscosity increases shown by these latices were generally lower than those of the LA-TZ latices examined previously. In particular, none of the HA latices gelled in the ZAAV test. The causes of these differences will be discussed below.

TABLE 2. COMPARISON OF POTENTIOMETRIC (ISO) AND CONDUCTIMETRIC KOH NUMBERS FOR HA LATICES

Latex sample	KOH No.	
	Potentiometric	Conductimetric
1	0.69	0.72
2	0.63	0.66
3	0.62	0.67
4	0.63	0.70
5	0.63	0.70
6	0.55	0.64
7	0.66	0.64
8	0.61	1.09
9	0.47	0.81
10	0.53	0.62
11	0.63	0.68
12	0.58	0.61
13	0.81	0.88
14	0.69	0.71
15	0.58	0.67
16	0.58	0.62
17	0.59	0.60
18	0.76	0.70
19	0.67	0.68
20	0.69	0.75
Mean value	0.63	0.71
CV (%)	12.3	15.9

Elemental Analyses

Measurements of the nitrogen, phosphorus, magnesium and potassium contents of each of these latices were also made (*Table 6*). In the case of potassium, measurements were made on the ultracentrifuged sera as well as the total solids films, in order to determine its distribution between serum and particle surface. Insufficient serum was available to permit the same approach with nitrogen and phosphorus analyses so the amounts of these elements associated with the particles were estimated for values obtained from centrifuged

cream, as described in the experimental section. These estimates are not considered to be very accurate and merely serve as a guide to the distribution of nitrogen and phosphorus between the two phases of latex. As with LA-TZ, the amount of non-ammoniacal nitrogen in these samples was quite consistent, averaging 0.29% of total solids with a fairly low coefficient of variation. The total phosphorus contents showed a fairly high variation and in all cases were higher than the levels indicated by the serum phosphate ion measurements. The phosphorus levels not accounted for by phosphate ion measurements were much higher

TABLE 3. COMPARISON OF VOLATILE FATTY ACID CONTENTS USING ISO METHOD (STEAM DISTILLATION) AND ION CHROMATOGRAPHY

Latex sample	VFA No.	
	ISO	Ion chromatography
1	0.10	0.08
2	0.10	0.08
3	0.04	0.03
4	0.03	0.03
5	0.03	0.03
6	0.06	0.05
7	0.03	0.06
8	0.05	0.07
9	0.06	0.05
10	0.05	0.03
11	0.09	0.04
12	0.05	0.02
13	0.19	0.21
14	0.04	0.07
15	0.12	0.10
16	0.04	0.07
17	0.07	0.06
18	0.06	0.03
19	0.05	0.02
20	0.08	0.12
Mean value	0.07	0.06
CV (%)	57.7	70.6

TABLE 4. VISCOSITY OF HA LATICES

Latex sample	Brookfield viscosity, 25°C			
	As received		At 59.0% d.r.c.	
	60 r.p.m.	6/60 r.p.m. ratio	60 r.p.m.	6/60 r.p.m. ratio
1	77.0	1.99	69.5	1.76
2	78.0	1.87	71.5	1.80
3	71.5	1.75	72.5	1.86
4	73.0	1.92	68.0	1.78
5	73.0	1.81	66.0	2.12
6	66.0	1.74	54.0	1.94
7	73.5	1.81	68.5	1.53
8	69.0	1.83	60.5	1.88
9	66.0	1.67	56.0	1.70
10	62.5	1.66	61.5	1.54
11	86.0	2.01	76.0	1.71
12	64.5	1.74	57.0	1.45
13	116.0	2.12	88.0	2.43
14	73.0	2.11	44.0	1.89
15	86.5	1.45	63.0	1.35
16	91.5	2.40	60.0	1.17
17	76.0	1.45	53.5	1.12
18	90.0	2.22	55.0	1.93
19	74.0	2.05	46.0	1.83
20	81.0	2.16	88.0	2.11
Mean value	77.4	1.89	63.9	1.75
CV (%)	15.8	13.1	18.5	18.3

and less variable than those of the LA-TZ latices.

The amounts of potassium found were moderately high, and contributed on the average a quantity equivalent to 44% of the ammonium ions measured by the conductimetric KOH titration. The results also show that the great majority of the potassium was associated with the serum, where its concentration is relatively constant, as noted by Resing and Lunshof⁷. On the average however, about 12.5% of the potassium appears to be associated with the particle surfaces, although the proportion varies between samples.

The magnesium contents of these latices showed considerable variation and the levels were generally higher than those found with LA-TZ latices but, again, showed no correlation with any stability index.

Serum Anion Concentrations

As described in an earlier paper⁶, ammonium-associated serum anion concentrations can be determined by KOH conductimetric titrations of latex serum samples. It is also possible to obtain a value for all serum anion concentrations other than soaps, proteins and amino acids by adding the contribution from ion chromato-

TABLE 5. ZST AND ZAAV STABILITY OF HA LATICES

Latex sample	ZST (s)	ZST/MST ratio	Viscosity ratio, 24 h/1 h	Viscosity ratio, 1 h/59% d.r.c.
1	150	0.147	1.95	1.99
2	180	0.167	2.17	1.71
3	165	0.154	2.28	1.88
4	220	0.170	2.67	1.99
5	200	0.172	2.67	2.05
6	270	0.196	2.61	2.98
7	150	0.170	2.81	2.23
8	195	0.165	2.62	3.09
9	350	0.216	1.48	1.30
10	335	0.240	2.19	1.45
11	265	0.235	1.47	1.25
12	173	0.162	2.10	1.15
13	145	0.204	1.29	1.39
14	195	0.171	1.19	1.57
15	255	0.236	1.09	1.27
16	255	0.176	1.06	2.17
17	265	0.178	1.52	2.52
18	195	0.226	1.44	1.64
19	287	0.178	1.28	1.39
20	218	0.257	1.36	1.02
Mean value	223	0.191	1.86	1.80
CV (%)	26.8	17.1	32.6	32.3

graphy results, carbonate ion measurements and hydroxyl ion concentrations calculated from pH values. The results, of these two types of measurement, expressed as millimoles KOH per 100 g rubber, are shown in *Table 7*. The results confirm previous conclusions that the chromatographic values are significantly lower than the conductimetric values, although the two methods correlate well. The discrepancy between the two methods is about 20% of the KOH titre, although the true difference is much greater because the KOH titration does not measure potassium-associated anions.

Variations in Specific Serum Anions

The individual concentrations of all the ions detected by ion chromatography have been measured together with the carbonate concentrations. The mean values and coefficients of variation for each of these ions are listed in *Table 8*.

These data show that the concentrations of the individual anions varied quite substantially from latex to latex although the citrate and malate levels were relatively consistent. As noted previously, the CV values of individual

TABLE 6. ELEMENTAL ANALYSES OF HA LATICES

Latex sample	Nitrogen (% of TS)		Phosphorous (p.p.m. of TS)		Magnesium (p.p.m. of TS)	Potassium (% of TS)	
	Total	Surface ^a	Total	Surface ^a		Total	Serum
1	0.26	0.15	375	190	36	0.18	0.15
2	0.26	0.14	355	200	41	0.17	0.14
3	0.24	0.15	252	246	20	0.22	0.14
4	0.31	0.15	330	137	12	0.21	0.17
5	0.30	0.15	315	91	10	0.21	0.17
6	0.38	0.12	327	231	28	0.20	0.15
7	0.28	0.13	313	108	25	0.18	0.15
8	0.30	0.14	361	157	29	0.20	0.19
9	0.32	0.15	393	390	31	0.16	0.14
10	0.28	0.13	405	111	31	0.18	0.15
11	0.30	0.15	518	96	100	0.18	0.17
12	0.30	0.14	465	454	90	0.18	0.12
13	0.22	0.18	363	204	15	0.23	0.17
14	0.33	0.15	352	211	62	0.19	0.18
15	0.20	0.11	360	265	15	0.17	0.17
16	0.29	0.12	552	156	22	0.20	0.16
17	0.29	0.14	299	143	13	0.20	0.15
18	0.25	0.15	480	130	70	0.20	0.22
19	0.33	0.15	550	220	97	0.18	0.16
20	0.34	0.16	510	125	17	0.18	0.18
Mean value	0.29	0.14	394	193	38	0.19	0.16
CV (%)	14.8	10.9	22.4	48.7	76.6	9.4	13.5

^aEstimated from elemental content of centrifuged cream

ions are much greater than that of the total ion concentration, as evidenced by the serum KOH titre values in *Table 7*.

Adsorbed Anion Concentrations

By subtraction of the serum KOH titre from the latex KOH titre the quantity of KOH equivalent to the ammonium-associated anions on the particle surfaces can be derived. The data for this calculation are given in *Table 9* where it is shown that the mean adsorbed anion titre is 2.73 mmoles KOH per 100 g rubber and its coefficient of variation is 60.7%, much

greater than the corresponding value for LA-TZ latices. It is also clear that 10%-20% of the ammonium ions in HA latices are associated with adsorbed anions and the remainder with the serum anions. These results again demonstrate, as for LA-TZ latices, that the variability of adsorbed anion titres is much higher than that of both total and serum anion values.

ZAA Titrations

The technique of titration with ammoniated zinc acetate solution (ZAA solution) was used

TABLE 7. TOTAL SERUM ANION CONCENTRATIONS OF HA LATICES

Latex sample	Anion concentration (mmoles KOH/100 g rubber)	
	Conductimetric	Separate ion determination
1	10.98	8.44
2	10.33	8.34
3	11.00	7.56
4	11.24	7.89
5	11.27	7.16
6	8.98	7.05
7	9.70	9.52
8	12.54	9.64
9	8.48	7.47
10	7.26	7.88
11	10.10	8.99
12	9.37	6.98
13	12.36	12.67
14	10.68	7.09
15	10.34	7.30
16	10.24	6.38
17	8.97	8.71
18	10.67	9.30*
19	10.35	8.63*
20	9.77	7.74
Mean value	10.23	8.24
CV (%)	12.2	16.9

TABLE 8. AVERAGE VALUES OF SERUM ANION CONCENTRATIONS

Anion	Mean concentration (mmoles/litre serum)	CV (%)
Carbonate	22.25	40.9
Acetate	12.81	91.9
Malate	9.28	34.5
Succinate ^a	5.45	65.4
Citrate	5.04	40.7
Formate	4.67	67.5
α Glycerophosphate	2.81	32.7
Glucose-1-phosphate ^b	2.24	43.5
Phosphate ^c	2.01	66.9
Oxalate	1.16	31.2
Chloride	1.10	89.8
Sulphate	0.58	50.2
Hydroxide	0.51	46.4

^a Not detected in eight latices (*Samples 3-7, 13, 16, 17*)

^b Not detected in *Sample 12*

^c Not detected in two latices (*Samples 19, 20*)

TABLE 9. CONDUCTIMETRIC KOH TITRES OF LATICES AND SERA

Latex sample	Titres (mmoles KOH/100 g rubber)		
	Latex	Serum	Surface
1	13.16	10.98	2.18
2	12.02	10.33	1.69
3	12.29	11.00	1.29
4	12.88	11.24	1.64
5	12.87	11.27	1.60
6	11.66	8.98	2.68
7	11.80	9.70	2.10
8	20.00	12.54	7.46
9	14.88	8.48	6.40
10	11.35	7.26	4.09
11	12.34	10.10	2.24
12	11.08	9.37	1.71
13	16.04	12.36	3.68
14	13.06	10.68	2.38
15	12.33	10.34	1.99
16	11.33	10.24	1.09
17	11.00	8.97	2.03
18	12.86	10.67	2.19
19	12.56	10.35	2.21
20	13.72	9.77	3.95
Mean value	12.96	10.23	2.73
CV (%)	16.0	12.2	60.7

to assess the total amount of soap in the latex⁶. Such measurements have been done on all of these latices and the results are shown in *Table 10*.

It can be seen that although the ZAA titres of latices and sera are moderately variable the difference between the two titres, expressed as adsorbed stearic acid content in the table, is very highly variable. This variability is even greater than that found with the independent measurement of total surface anions described above. The significance of these results will be discussed later.

Electrical Conductivity

The electrical conductivities of each latex, after dilution to 30% d.r.c. with its own serum, and of each serum sample have been measured and the results are shown in *Table 11*. The electrical conductivities of the HA latices and their sera did not vary greatly between samples. This conclusion is consistent with the measurements of total serum anion concentrations (*Table 7*) which also revealed relatively low coefficients of variation.

It can be shown that at a d.r.c. of 30%, *i.e.* a dispersed phase volume fraction of 0.3226, the ratio of the serum conductivity to that of the latex would be 1.71 if the particle surface conductivity was negligible⁶. This ratio, designated CR30, has been calculated for all these latices and is shown in *Table 11*. In most cases the measured ratio was close to 1.71 indicating that electrical double layer conductivity was zero or negligibly small. Only about three of the latices (*Samples 2, 3 and 16*) can be considered to differ significantly from the theoretical value, compared with eight out of twenty-one LA-TZ latices¹.

Comparison of HA and LA-TZ Latices

In many properties, *i.e.* TSC, d.r.c., KOH number, viscosity, non-rubber solids content (NRS), alkalinity, pH and MST, HA and LA-TZ latices show similar variabilities and, except for alkalinity and pH, similar average values. As noted above, the VFA numbers of HA latices however, tend to be higher and more variable than those of the LA-TZ latices tested previously. This confirms the efficacy of the zinc oxide/tetramethylthiuram disulphide system as a preservative for latex.

HA latices appear less stable to zinc ions than LA-TZ latices when judged by their ZST values or ZST/MST ratios but appear much more stable in the ZAAV test. The latter effect is probably attributable to the higher ammonia content of the HA latices as the addition of ammonia to LA-TZ latices produces measurable improvements in ZAAV values (*Table 12*).

TABLE 10. TITRATIONS WITH AMMONIATED ZINC ACETATE SOLUTION

Latex sample	Latex titre (mmoles Zn/100 g rubber)	Serum titre (mmoles Zn/100 g rubber)	Surface titre as stearic acid (g/100 g rubber)
1	0.71	0.60	0.06
2	0.15	0.01	0.31
3	1.48	1.30	0.10
4	2.76	2.20	0.31
5	2.09	1.80	0.17
6	1.17	0.12	0.60
7	1.46	1.20	0.14
8	3.97	2.50	0.82
9	2.68	1.70	0.55
10	1.42	0.97	0.26
11	1.92	1.50	0.24
12	1.89	1.50	0.23
13	3.48	1.90	0.89
14	2.10	1.60	0.28
15	2.52	2.20	0.14
16	3.76	3.70	0.00
17	3.19	2.90	0.40
18	3.18	2.33	0.48
19	2.93	2.30	0.27
20	3.98	2.15	1.04
Mean value	2.34	1.72	0.36
CV (%)	46.4	51.8	78.2

The total serum anion concentrations tend to be a little higher for HA latices than for LA-TZ latices, but the differences are not large. Glucose-1-phosphate was detected in nineteen of the twenty HA latices but in only six of the twenty-one LA-TZ latices.

Latex Processability

The data presented in *Tables 1-11* represent the measurement of over forty parameters for twenty HA latex samples. This permits the summarising of properties and composition of a 'typical' HA latex, as it may reasonably be assumed that these samples are representative

of current commercial imports into Europe. Such a summary is set out in *Table 13*.

Many of the conventional properties, as given in *Tables 1-3*, show that HA latex is a consistent latex with properties that do not vary widely. However, of central interest in this study are the results given in *Table 5* which relate to the processability of the latices. As with LA-TZ latices, the ZST values are seen to relate strongly to the MST results whereas the ZAAV viscosity increase figures appear to be completely unrelated. The concentration of aqueous phase ammonium ions would be expected to influence stability to zinc but clearly it is not the

TABLE 11. ELECTRICAL CONDUCTIVITIES OF HA LATICES AND SERA

Latex sample	Conductivity (mmhos, 25°C)		Conductivity ratio (CR 30)
	Latex (30% d.r.c.)	Serum	
1	8.68	14.33	1.65
2	8.68	13.98	1.61
3	8.77	13.60	1.55
4	9.47	16.10	1.70
5	9.56	15.30	1.60
6	8.88	15.10	1.70
7	9.42	16.10	1.71
8	9.42	16.10	1.71
9	7.89	13.50	1.71
10	8.36	14.30	1.71
11	10.88	18.60	1.71
12	8.45	14.45	1.71
13	10.88	18.60	1.71
14	8.80	15.40	1.75
15	9.16	15.20	1.66
16	9.33	15.30	1.64
17	8.35	14.20	1.70
18	10.67	19.10	1.79
19	9.86	17.25	1.75
20	9.48	16.50	1.74
Mean value	9.25	15.65	1.69
CV (%)	9.0	10.60	3.4

TABLE 12. EFFECT OF ADDITION OF AMMONIA TO AN LA-TZ LATEX ON ITS ZAAV VISCOSITY INCREASE

Ammonia content (% of aqueous phase)	ZAAV ratio (24 h : 1 h)
0.5 (as received)	2.84
0.8	1.76
1.0	1.50
1.3	1.47
1.7	1.49
2.0	1.11

dominant factor, possibly because it is relatively constant.

The ZAAV ratio shows a moderately high coefficient of variation but is much less variable than that of the LA-TZ latices examined earlier. This indicates either that HA latices are inherently less variable, in their response to zinc ions, than LA-TZ latices or that the ZAAV test is less discriminating with HA latices due to their higher ammonia contents. In further contrast to LA-TZ latices, the ZAAV ratios for HA latex do not suggest any significant correlation with either KOH surface titres or

TABLE 13. COMPOSITION AND PROPERTIES OF A 'TYPICAL' COMMERCIAL HA LATEX

Item	Latex (% by weight)	Total solids film (% by weight)
Rubber ^a	59.67	97.61
Protein, <i>etc.</i> ^b	1.06	1.73
Soaps ^c	0.23	0.38
Salts	0.40	0.28 ^d
Ammonia	0.68	—
Water	37.96	—
TSC (%)	61.31	—
D.r.c. (%)	59.67	—
Non-rubber solids (%)	1.64	—
pH	10.65	—
Alkalinity (% aqueous phase)	1.76	—
MST (s)	1168	—
VFA No.	0.07	—
KOH No.	0.63	—

^a As measured by d.r.c.

^b Includes carbohydrates, amino acids, sugars

^c Calculated as ammonium stearate

^d Assuming carbonate, acetate and formate are volatilised

ZAA surface titres. In fact, no immediately obvious correlation can be found for the ZAAV ratios of HA latices, which leaves the cause of the variations obscure at present. It appears that a combination of several factors may be determining the ZAAV ratio but the nature of these factors has yet to be determined. They could, for example, include the influence of the nature of the adsorbed soaps, as at least five different fatty acid soaps are known⁸ to be present in latex. The current study is being extended to improve the techniques for determining the soap level on the latex and on the particle surface, and to identify its various components.

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Epoxidised Natural Rubber

C.S.L. BAKER*, I.R. GELLING* AND AZEMI BIN SAMSURI*

The reaction of natural rubber with peracids yields a new polymer, the properties of which depend on the degree of epoxidation. The epoxide groups are randomly distributed along the rubber backbone and this together with the stereo-specific nature of the epoxidation reaction and the relatively small size of the oxygen atom, result in a polymer that can strain crystallise and, hence has good strength properties. Hysteresis and resistance to hydrocarbon oils increase with the degree of epoxidation whereas air permeability decreases. At epoxide levels of 50 mole per cent, these properties are comparable to those of some of the speciality synthetic elastomers. Excellent reinforcement of epoxidised natural rubber is obtained with silica fillers, even in the absence of coupling agents. Two levels of epoxidation, 25 mole per cent (ENR-25) and 50 mole per cent (ENR-50), have been studied for their potential as commercial rubbers, and both are available as development materials.

The mechanical properties of natural rubber (NR) are generally superior to those of many synthetic elastomers. However, NR cannot compete with speciality synthetic rubbers such as the butyls and nitriles with regard to gas permeability and oil resistance. The chemical modification of NR has been studied for many years, both as a means of changing the properties of the polymer and as a route to other useful innovative concepts such as bound antioxidants¹, Novor crosslinking systems², comb grafts³ and silica coupling agents⁴. To be commercially viable the technical improvements achieved by modification of NR must also be economically attractive.

The epoxidation of NR and other unsaturated polymers has been reported in the literature^{5,6,7}. However, there is little data available on the properties of the products and in some cases the results are conflicting. It has been claimed that epoxidation of unsaturated polymers increases wear and improves solvent resistance, tensile strength and other mechanical properties⁷, whereas other workers have reported a reduction in strength properties^{8,9}.

Epoxidation is an economically attractive method of modifying NR since it is an established industrial method and it utilises cheap reagents.

The epoxidation of NR latex has been studied¹⁰ over a range of reaction conditions and the products characterised. Unless the reaction conditions are carefully controlled secondary ring-opening of the epoxide groups can occur and it is the presence of these structures that is responsible for the conflicting property reports in the literature. Under controlled conditions specific levels of epoxidised NR (ENR) are obtained. ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy shows that these materials are free from any other chemical modifications. The latter technique was also employed¹⁰ to study the distribution of epoxide groups along the NR backbone. Even though these materials were prepared from NR latex in a two-phase system, the epoxide groups were found to be randomly distributed along the NR molecule.

The glass transition temperatures (*T_g*) of ENR, as measured by differential scanning calorimetry, were single sharp events and the value increased by approximately 1°C per mole per cent epoxidation.

The physical properties of a range of ENR vulcanisates will be discussed with particular emphasis on their strength properties.

*Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford, United Kingdom

EXPERIMENTAL

All vulcanisates were prepared by standard techniques. The gum formulation was mixed on a two-roll mill and all filled compounds in a Size B Laboratory Banbury at 116 r.p.m. starting at 50°C using the following mix cycle:

0 min : Add rubber (ENR compounded with 0.25 p.h.r. sodium carbonate)

1 min : Add powders (zinc oxide, stearic acid, antioxidant, etc.)

1½ min : Add ½ black and process oil

2½ min : Add remainder of black

3½ min : Sweep down feed chute

4 min : Dump

In all cases, the sulphur and accelerators were added later on a two-roll mill and the mixes cured to optimum at 150°C, unless otherwise stated.

The formulations employed are shown in Tables 1 and 2.

The following physical testing procedures were employed:

- Tensile strength to ISO 37
- Hardness to ISO 48 (ASTM D1315)
- Resilience, Dunlop triposometer, to BS 903 : Part A8
- Ring fatigue to ISO 6943
- Tear strength, trouser to ISO 34
- Air permeability to ISO 1399
- Volume swelling to ISO 1817 (ASTM D471)
- Abrasion, Akron to BS 903 : Part A9 Method C.

Rolling Resistance Testing

Rolling resistance was measured from the power consumption of the test tyres under load on a Heenan Froude test rig less the power with the same tyre in skimming contact with the

TABLE 1. COMPOUND FORMULATIONS

Compound	Formulation			
	1	2	3	4
Polymer	100	100	100	100
Carbon black (N220)	—	Varies	50	—
Ultra-Sil VN3	—	—	—	50
Aromatic oil	—	5	5	5
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Antioxidant ^a	2	2	2	2
S	1.5	1.5	1.5	1.5
MBS	1.5	1.5	1.5	1.5
DPG	—	—	—	0.5
CTP ^b	—	0.2	—	—

^a Poly-2,2,4-trimethyl-1,2-dihydroquinoline

^b N-Cyclohexylthiophthalimide

TABLE 2. TYRE TREAD FORMULATIONS

Compound	Formulation			
	6	7	8	9
NR (SMR L)	100			
SBR 1712		100		
ENR-25			100	100
ISAF N220	50	50	25	15
Ultra-Sil VN3	—	—	25	35
Process oil	4	—	4	4
Antioxidant ^a	2	2	2	2
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Sulphur	1.5	1.8	2.4	2.4
TBBS	1.5	0.7	1.0	1.2
CTP ^b	0.1	—	0.2	0.1

All tyres were cured at 150°C for 40 min

^a N(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

^b N-Cyclohexylthiophthalimide

wheel (1.71 m diameter). Initially, all the tyres were conditioned by subjection to a 60 min run-in period at 80 km per hour and 80% of rated load. Inflation pressure was set at 248 KPa

(cold) and the tyres (165 × 13) were run to equilibrium temperature conditions for 45 min at 80% of the rated load for the two speeds of test (48 km and 80 km per hour). Three power measurements per tyre were recorded at 15 min intervals for each speed, and the relative ratings calculated from average power readings.

The tearing energy T was calculated from the equation:

$$T = \frac{(\delta w)}{(\delta A)_t} = \frac{2F\lambda}{t} - wE$$

where F is the force applied to each leg of the trouser test piece

t is the sample thickness

w is the sample width

λ is the extension ratio

E is the strain energy per unit volume in the legs of the test piece.

Wide test pieces were employed so $\lambda \approx 1$, $E = 0$ and tearing energy $T = \frac{2F}{t}$.

RESULTS AND DISCUSSION

ENR can be crosslinked using any of the standard sulphur formulations normally employed for NR or by a peroxide system¹¹. However, a conventional cure system based on 2.5 p.h.r. sulphur and 0.5 p.h.r. sulphenamide results in vulcanisates with poor ageing characteristics¹². Sulphur acids produced by the oxidation process attack the epoxide groups ultimately causing crosslink formation, which results in a substantial increase in modulus and consequent reductions in elongation at break and tensile strength. It is, therefore, recommended that all epoxidised NR formulations should contain a base to neutralise these acids and hence improve ageing properties.

Typical cure curves of ENR-25 (25 mole per cent epoxidised NR) and ENR-50 (50 mole per cent epoxidised NR) in a semi-EV formulation (Table 1, Formulation 1) are shown in Figure 1.

It is well recognised that the dissipative processes which occur in rubbers are important

factors in determining their strength. The strength of strain-crystallising rubbers is substantially superior to that of non-strain-crystallising materials, where the dissipative process is predominantly visco-elastic. NR has a stereo-regular structure and hence can undergo strain crystallisation. This is especially reflected in the strength properties of NR gum vulcanisates. The epoxidation process is a stereo-specific reaction¹³ and ENR will thus retain the stereo-regular *cis* 1,4-configuration of NR. This, together with the relatively small size of the oxygen atom, suggest that ENR may also undergo strain crystallisation as only minor geometrical rearrangements of the crystalline molecular packing are necessary for the inclusion of the epoxy group. The tensile strength of gum ENR vulcanisates compared to NR and a non-crystallising acrylonitrile-butadiene copolymer (NBR) supports this view which has been confirmed by X-ray data¹⁴ (Table 3).

The general physical properties of black-filled ENR vulcanisates are recorded in Table 4. As expected, resilience decreased with increasing epoxide content and high tensile strength was observed. However, for strain-crystallising rubbers the tear strength was low and the non-relaxing fatigue decreased with increasing epoxide level, although that of ENR-50 was still nearly an order of magnitude greater than that of the non-crystallising NBR vulcanisate.

In view of these results, the strain-crystallisation dependent properties of ENR have been examined in more detail. As reinforcing fillers have a pronounced effect on the tear strength of rubbers, the initial work was carried out on gum vulcanisates.

Non-strain-crystallising rubbers such as SBR and NBR tear in a time-dependent manner when subjected to a constant load; whereas, with strain-crystallising rubbers, tear is independent of time below their critical tearing energy. Above this value, catastrophic tearing occurs. NR, ENR-25 and ENR-50 gum vulcanisates all exhibited a critical tearing energy as expected for strain-crystallising rubbers. No time-dependent crack growth was observed but above the critical tearing energy, tear was catastrophic. The effects of tearing rate and

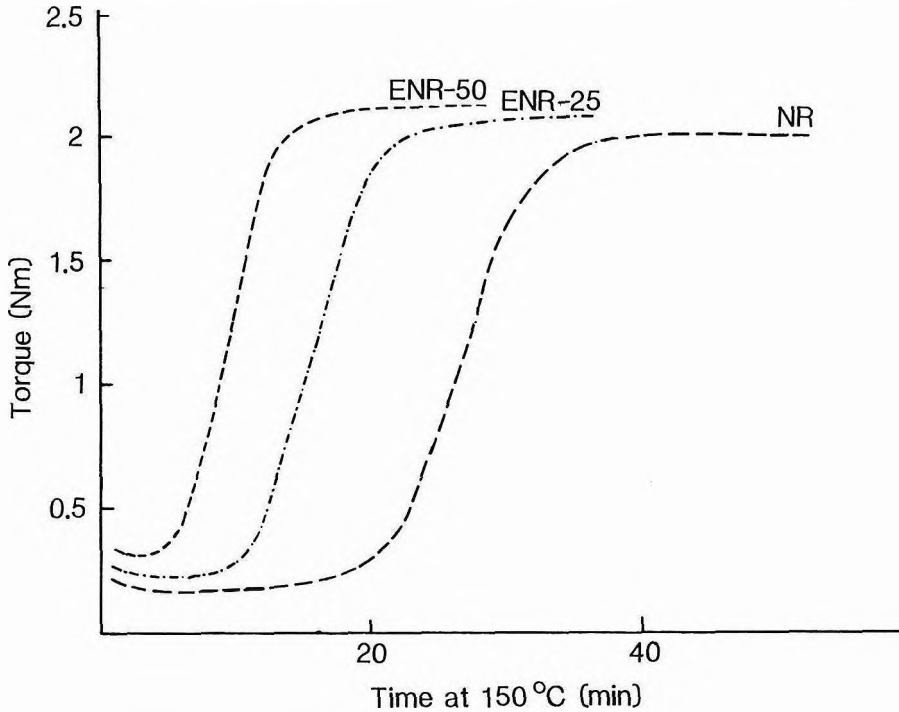


Figure 1. Monsanto rheographs of NR, ENR-25 and ENR-50 in a semi-EV formulation (Formulation 1, Table 1).

temperature on the strength of vulcanisates of similar moduli are shown in Figures 2 and 3. This data strongly supports the view that ENR like NR strain crystallise in contrast to such polymers as SBR. However, it was noted that the ENR-50 values were significantly lower than those of NR and ENR-25, which may indicate a reduced degree of crystallinity in this case.

None of the above results explain the observed low tear strength of ENR in black-filled (30 p.h.r.

N220) vulcanisates (Table 3). High tear strength is normally associated with 'knotty' tearing which depends on the rate, temperature, the type and level of black filler and the degree of anisotropy¹⁵. To date, only a limited study of these variables has been carried out, but high ENR tear strength in black-filled systems can be achieved. The effect of black (N220) level on the tearing energy of NR, ENR-25, ENR-50, SBR and NBR vulcanisates is recorded in Figure 4 at a test piece extension rate of 10 mm

TABLE 3. TENSILE STRENGTH OF GUM VULCANISATES (FORMULATION 1)

Property	Gum vulcanisate			
	NR	ENR-25	ENR-50	NBR ^a
Tensile strength (MPa)	29.0	31.0	25.0	12.4
Modulus at 100% extension (MPa)	0.93	0.92	0.89	1.12
Modulus at 300% extension (MPa)	2.29	2.23	2.13	1.83
Elongation at break (%)	665	680	660	630

^a 34% acrylonitrile content

TABLE 4. PHYSICAL PROPERTIES OF ENR VULCANISATES COMPARED TO NR AND NBR VULCANISATES (FORMULATION 2, TABLE 1, 30 P.H.R. N220 BLACK)

Property	Vulcanisate			
	NR	ENR-25 ^a	ENR-50 ^a	NBR ^b
Mooney scorch, t_5 at 120°C (min)	48	30	25	20
Time to optimum cure at 150°C (min)	24	17	23	50
Tensile strength (MPa)	30.6	28.4	28.3	15.3
Modulus at 100% extension (MPa)	1.53	1.83	1.95	2.2
Modulus at 300% extension (MPa)	7.7	8.9	8.8	9.5
Elongation at break (%)	660	590	580	365
Hardness (IRHD)	56	57	64	61
Resilience, Dunlop at 23°C (%)	76	66	19	32
Compression set, 24 h/70°C (%)	21	22	30	17
Ring fatigue				
0%-100% extension (kcs)	103	165	250	38
50%-150% extension (kcs)	1 300	1 200	330	35
Tear strength, trouser (kN/m)	16	8	7	9
Abrasion, Akron (mm ³ /500 rev.)	22	14	12	11
Goodrich HBU, 5.7 mm stroke, 10.9 kg load from 23°C for 30 min, ΔT (°C)	40	40	42	88

^a Formulation includes 0.25 p.h.r. sodium carbonate

^b 34% acrylonitrile content

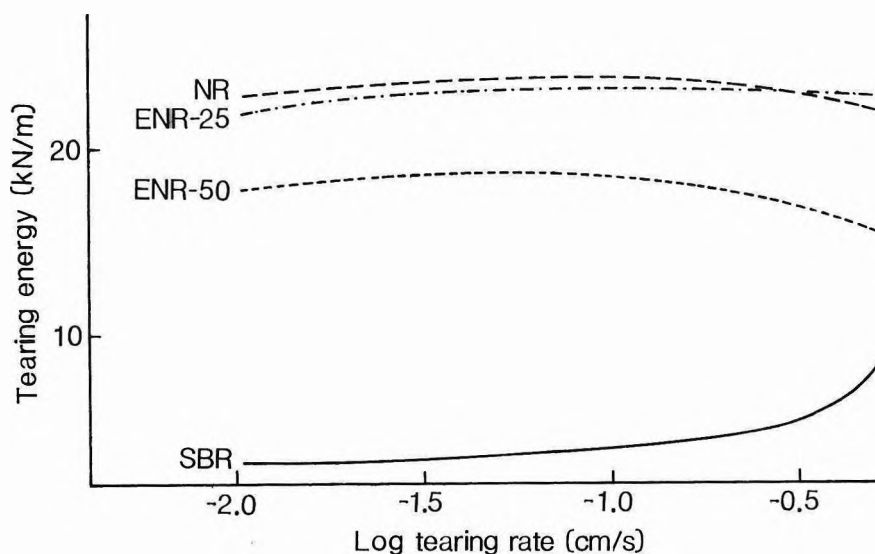


Figure 2. Plot of tearing energy against rate at 23°C for gum vulcanisates (Formulation 1).

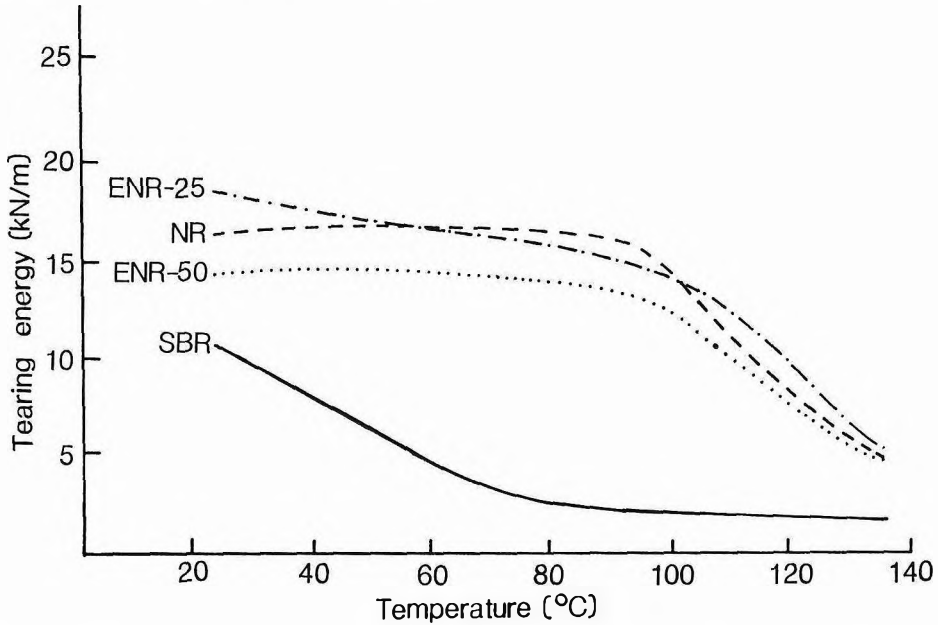


Figure 3. The effect of temperature on tearing energy of gum vulcanisates (Formulation 1). Tear rate $\log -0.78$ cm per second.

per minute and 23°C. Below 40 p.h.r. of black the tearing energy of ENR-25 and ENR-50 is low, but beyond this point, a substantial increase occurs. A similar increase was observed with NR, whereas the tearing energy of the non-crystallising rubbers decreased. At a faster test rate, 500 mm per minute, the tear energy of ENR-25 at high black loading was 50% higher than that of NR.

The different behaviour of ENR in black-filled systems cannot be due to a lack of general reinforcement as other properties e.g. tensile modulus and modulus contradict this view. It is unlikely that the black filler interferes with the strain crystallisation process as this does not occur with NR¹⁵ and non-relaxing fatigue data (Figure 5) indicate that strain crystallisation still occurs in ENR black-filled vulcanisates. It was noted that the carbon black dispersion of many of the ENR vulcanisates was poor in comparison to the other rubbers, and this may well result in inadequate anisotropy to enhance knotty tear. Alternative processing techniques are currently being investigated to check this idea.

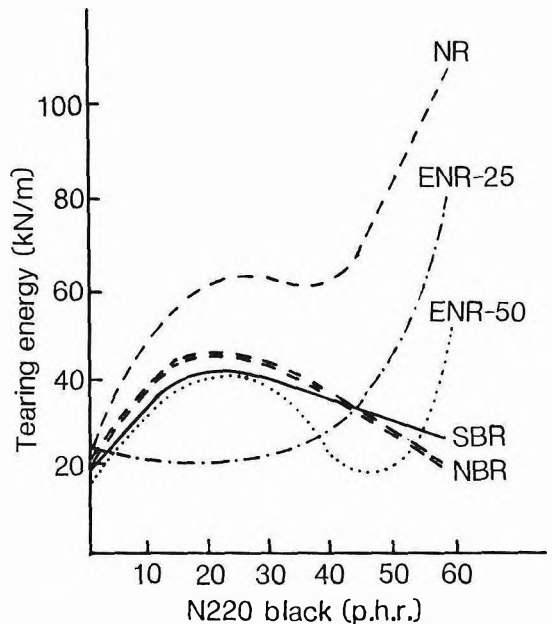


Figure 4. The effect of black (N220) loading on the tear energy of vulcanisates (Formulation 2).

TABLE 5. OIL RESISTANCE OF ENR VULCANISATES COMPARED TO NR, CR AND NBR

Property	Polymer				
	NR	ENR-25	ENR-50	CR	NBR
Percentage volume swelling (70 h/100°C)					
ASTM No. 1 oil	97	16	-2	3	-4
ASTM No. 2 oil	141	86	13	33	6
ASTM No. 3 oil	235	167	39	59	26
Percentage retention of tensile strength (70 h/100°C) in ASTM No. 3 oil	9	22	72	51	78

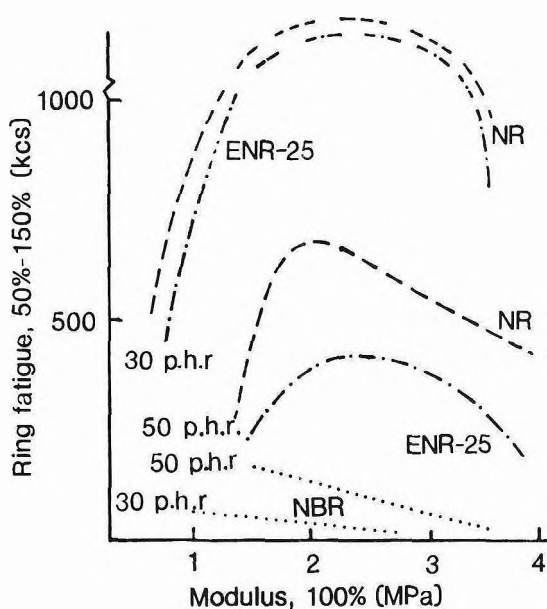


Figure 5. Non-relaxing fatigue properties of NR, ENR-25 and NBR vulcanisates (Formulation 2).

The epoxidation of NR also results in a considerable increase in oil resistance and reduction in gas permeability. Swelling tests in a series of standard oils have demonstrated that at the 25 mole per cent epoxidation level there is a substantial improvement over NR and at 50 mole per cent epoxidation the oil resistance is comparable to those of some of the speciality synthetic elastomers. Table 5 compares the oil

resistance properties of ENR with those of NR, polychloroprene (CR) and a medium NBR (34% acrylonitrile content). The oil resistance of ENR-50 falls between those of polychloroprene and NBR.

Similar improvements are observed with regard to gas permeability. The air permeability of ENR-25 and ENR-50 are compared to those of other polymers in Table 6.

Another distinctive feature of ENR is the high reinforcement obtained with silica fillers. Silica reinforces ENR-25 and ENR-50 to an equal extent to that obtained with carbon black without the addition of a silane coupling agent. The comparative properties of silica-filled and black-filled NR and ENR are demonstrated in Table 7. The relative low reinforcement of the

TABLE 6. COMPARATIVE AIR PERMEABILITIES OF RUBBERS AT 30°C

Rubber	Air permeability ^a
NR ^a	100
ENR-25	32
ENR-50	8
SBR-1500	48
Butyl	6
NBR (39% ACN content)	4

^a NR value taken as 100 and other results rated accordingly

TABLE 7. COMPARISON OF BLACK-FILLED AND SILICA-FILLED VULCANISATES (FORMULATIONS 3 AND 4)

Property	NR		ENR-25		ENR-50	
	Black	Silica	Black	Silica	Black	Silica
Time to optimum cure at 150°C (min)	22	35	17	30	19	32
Hardness (IRHD)	65	69	69	67	73	68
Tensile strength (MPa)	29.4	23.2	25.4	21.0	24.5	22.4
Modulus at 300% (MPa)	11.9	5.8	12.4	12.8	13.5	12.6
Elongation at break (%)	495	720	435	405	500	435
Abrasion, Din (mm ³)	199	364	212	250	278	289
Abrasion, Akron (mm ³ /500 rev.)	21	63	14	15	11	14
Compression set, 24 h/70°C (%)	18	32	17	18	21	22
Ring fatigue, 0%-100% (kcs)	70	51	65	52	93	58
Goodrich HBU, 5.7 mm stroke, 10.9 kg load from 23°C for 30 min, ΔT (°C)	7	47	7	7	23	19

silica-filled NR vulcanisate is reflected in the lower modulus, increased abrasion and higher Goodrich heat build-up. In contrast neither ENR-25 nor ENR-50 show any significant variation in these properties on changing from 50 parts N330 to 50 parts silica.

With increasing levels of epoxidation hysteresis also increases and this is reflected in increased wet grip and lower resilience at ambient temperatures. Both these properties are important tyre tread parameters and it has been shown¹⁶ that, with general-purpose rubbers, improved wet grip usually results in increased rolling resistance. However, at elevated temperatures the hysteresis of ENR-25 compounds decreases (*Figure 6*) and hence the rolling resistance decreases. Thus, the relatively cool tyre surface in contact with a wet road should exhibit good wet grip, while the bulk of the tread at higher temperature will have low rolling resistance.

Tyres retreaded with a series of ENR compounds have been examined for wet grip by recording skid path lengths using a two-

wheel Schallamach trailer¹⁷. Rolling resistance has also been measured on a Heenan Froude test rig. The results are recorded in the form of a Morton and Krol plot in *Figure 7*. Clearly, the ENR compounds have both high wet grip and low rolling resistance, and therefore have potential as tyre tread compounds¹¹.

CONCLUSIONS

Natural rubber can be epoxidised at the latex stage to yield a new polymer — ENR. With increasing epoxide content, oil resistance and hysteresis increase, and gas permeability decreases. But unlike many synthetic polymers with similar properties, ENR can strain crystallise. A high degree of reinforcement is obtained with silica fillers in the absence of coupling agents.

These properties suggest a wide range of potential applications for ENR many of which are being evaluated e.g. tyres, belting, oil hose, seals, various engineering applications including mountings and shoe soling.

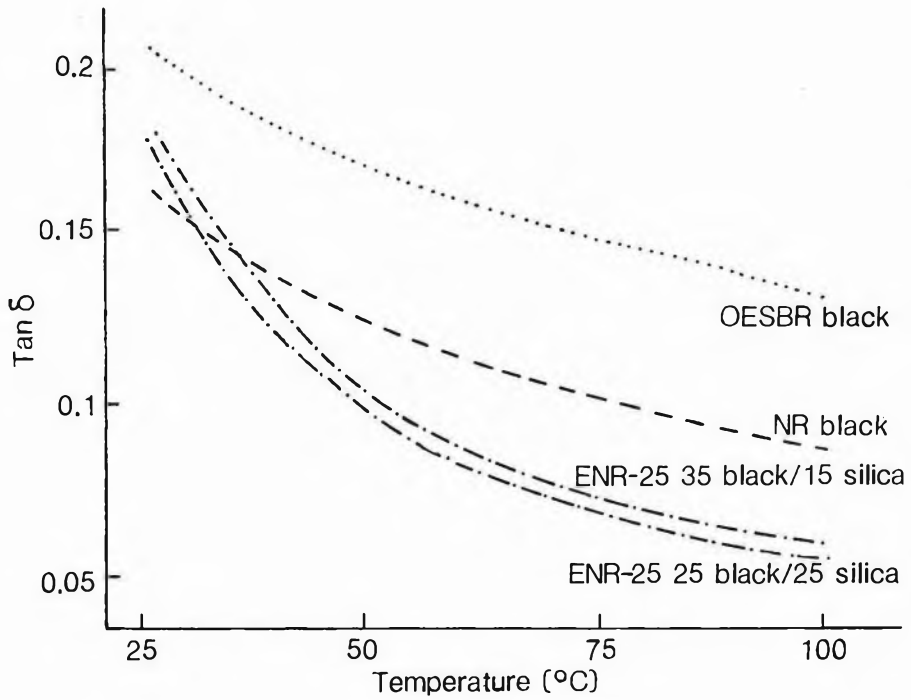


Figure 6. The effect of temperature on the hysteresis properties of tyre tread compounds (Formulations 6-9). Obtained from the Dunlop rotary power loss test.

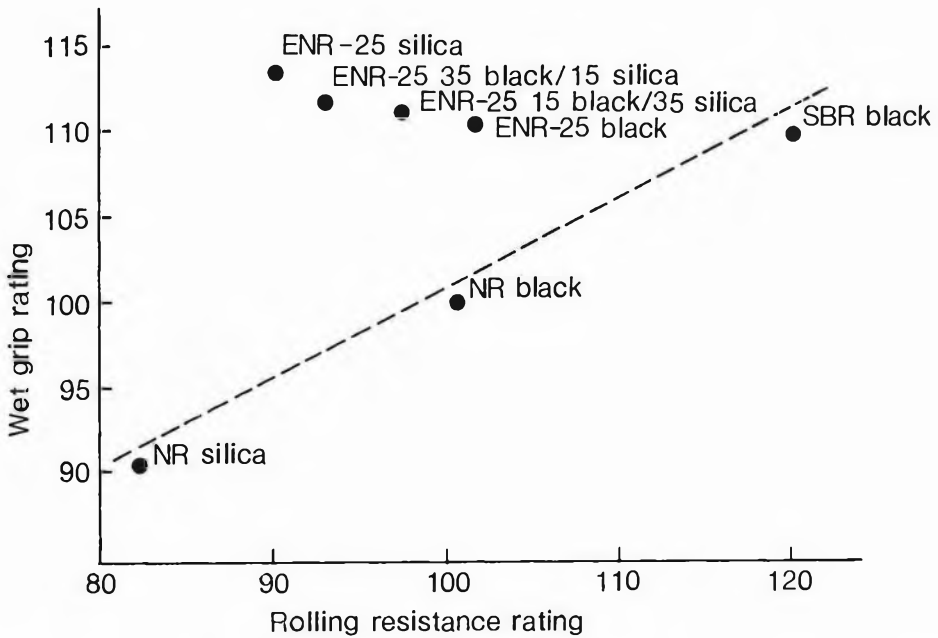


Figure 7. Wet grip/rolling resistance ratings of steel radial tyres retreaded with various rubbers.

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